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The ground state of solid helium three.

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THE GROUND STATE OF SOLID HELIUM THREE

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CHAPTER I

DESCRIPTION OF SOLID HELIUM

Rare Gas Solids

The physical properties of the solid phases of the "rare gas" elements are of particular interest because their atomic electrons occupy fully closed shells, and the only chemical binding force is the weak van der Waals interaction. The physical properties of these solids are thus in many respects more open to analysis than most other solids. Further, the weakness of the interparticle force gives rise to definite quantum-mechanical effects in the motion of the atoms in the condensed state.

Dobbs and Jones[1] have written an extensive review of the experimental and theoretical work on these solids, with emphasis on solid argon. They show the importance of the quantum-mechanical zero-point energy by listing the ratio of zero-point energy to cohesive energy for the rare gases (listed in order of decreasing atomic weight): xenon, 0.031; krypton, 0.054; argon, 0.097; neon, 0.311; helium four, 3.92. Hence, ordinary classical lattice dynamics applies to xenon, krypton, and argon, with small quantum-mechanical corrections. Neon can be treated adequately by including anharmonic terms in the interatomic potential. However, helium is of such low atomic mass that more powerful techniques must

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[1] E. R. Dobbs and G. O. Jones, Theory and Properties of Solid Argon. Reports on Progress in Physics, Vol. XX, 516 (1957).

[illegible]

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[illegible]

be employed.[2] Further, there is also an isotope of atomic weight three, which has spin 1/2 and obeys the Fermi-Dirac statistics.

This thesis is directed to the task of describing the ground state of He^3 in a way which includes quantum effects in the basic formalism. The description of the ground state will be used in turn to calculate physical quantities which will be compared with experimentally observed quantities.

Bernardes and Primakoff[3] (hereafter termed B.P.) have presented a theory of solid He^3 and have drawn extensive conclusions from their approximate ground-state wave function. The present work is mainly an attempt to give a more accurate description of the ground state than the formulation of B.P.

Properties of Atomic and Solid Helium

Solid He^4 possesses no such startling properties as the liquid phase. There has been no such intensive application of powerful theoretical tools to the solid, as there has been to the liquid. However, much experimental work has been performed, and theoretical explanation made of the observed results. Several reviews of the properties of solid He^4 have been published.[2,4,5]

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[2] C. Domb and J. S. Dugdale, Solid Helium. Progress in Low Temperature Physics, Vol. II (C. J. Gorter, editor Interscience Publishers, New York, 1957) p. 33[illegible].

[3] N. Bernardes and H. Primakoff, Phys. Rev. 119, 968 (1961).

[4] F. London, Superfluids, Vol. II (Wiley and Sons, New York, 1954).

[5] K. R. Atkins, Liquid Helium (Cambridge University Press, Cambridge, 1959).

Since 1948, He^3 has been made available in increasing amounts, and there has been considerable recent work with this isotope. Broad discussion of the properties of liquid and solid He^3 is contained in several sources.[4,5,6,7,8,9,10,11]

The nuclear moment of He^3 is - 2.1274 nuclear magnetons. Its atomic mass (on the O^{16} scale) is 3.01693, while that of He^4 is 4.00388. Properties which are directly due to the atomic electrons are the same for the two isotopes aside from an extremely small effective mass correction. These effects include atomic spectra and the interatomic potential.

At atmospheric pressure, He^3, like He^4, remains liquid at absolute zero temperature. Crystallization takes place on application of about 30 atm of pressure. A pressure of twenty-five atm is needed to solidify He^4.

The properties of solid He^3 have not been thoroughly explored experimentally. Much nuclear resonance experimentation has been carried

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[6] E. F. Hammel, The Low Temperature Properties of Helium Three. Progress in Low Temperature Physics, Vol. I (C. J. Gorter, editor, Interscience Publisher, New York, 1937), p. 78.

[7] V. P. Peshkov and K. N. Zinoveva, Reports on Progress in Physics, Vol. XXII, 504 (1959).

[8] Proceedings of the Symposium on Solid and Liquid Helium Three (Ohio State University, 1957).

[9] Helium Three (J. G. Daunt, editor, Ohio State University Press, Columbus, Ohio, 1960).

[10] Proceedings of the Seventh International Conference on Low Temperature Physics (G. M. Graham and A. C. Hollis Hallet, editors, University of Toronto Press, 1961), p. 583.

[11] E. R. Grilly and E. F. Hammel, Liquid and Solid He^3. Progress in Low Temperature Physics, Vol. III (C. J. Gorter, editor, to be published).

out. W. M. Fairbank has reviewed this work.[9,10,11] Data on the PVT relationships near the melting curve have been published by E. R. Grilly, S. G. Sydoriak, and R. L. Mills,[9] and by Grilly and Mills.[12] Data on thermal conductivity have been published by E. J. Walker and H. A. Fairbank.[9]

Schuch, Grilly and Mills,[13] through X-ray diffraction, have found that solid He^3 exists in two phases. The so-called α phase, a body-center cubic configuration, exists at pressures below about 100 atm, and the β phase, of hexagonal close-packed structure, exists at higher pressures. This phase transition was also observed by Grilly and Mills,[12] as a systematic discontinuity in the specific volume.

Preliminary measurements of specific heat of the solid have been made by Edwards, Baum, Brewer, Daunt and McWilliams.[9] The pressure-temperature dependence of the melting curve has been obtained to 0.06° K by the same group. They find the entropy to have a constant value close to $R\ln 2$ over the range 0.07° K to 0.7° K.

The principal anomaly in the behavior of the solid lies in a minimum in the melting pressure curve, plotted as a function of temperature, at $p = 29.3$ atm, $T = .32°$ K. The existence of the minimum is accompanied by interesting effects, including a negative thermal expansion coefficient, and the consequent possibility of melting the solid by lowering its temperature at constant pressure. By the Clausius-Clapeyron equation

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[12] E. R. Grilly and R. L. Mills, Ann. Phys. 8, 1, (1959).

[13] A. F. Schuch, E. R. Grilly, and R. L. Mills, Phys. Rev. 110, 775 (1958).

$$\left.\frac{dP}{dT}\right)_{melt} = \frac{S_{liq} - S_{sol}}{V_{liq} - V_{sol}}$$

The existence of higher thermodynamic order in the liquid than in the solid would yield such behavior.

The Helium Interparticle Potential and

The Many Body Hamiltonian

The stationary states of an aggregate of helium atoms are solutions of the Schrodinger equation

$$H_{He} \Psi_n = E_n \Psi_n , \qquad (1)$$

where H_{He} is the many body Hamiltonian involving all the nucleii and all the electrons of the solid:

$$H_{He} = - \sum_{i=1}^{K} \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{a=1}^{N} \frac{\hbar^2}{2M} \nabla_a^2 + \frac{1}{2} \sum_{i,j}' \frac{e^2}{r_{ij}}$$

$$+ V_{ai}(X_1 \ . \ . \ . \ X_N \ y_1 \ . \ . \ . \ y_K) + V_{aa}(y_1 \ . \ . \ . \ y_K). \qquad (2)$$

Here i labels one of the K electrons, a labels one of the N nucleii, the X_i label all the coordinates (including spin) of electron i. Nuclear coordinates are described by the y's. V_{ai} and V_{aa} are the nucleus-electron and nucleus-nucleus potential energy.

Following the adiabatic approximate of Born and Oppenheimer,[14] we separate ψ into a part depending upon electron coordinates that contains

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[14] M. Born and J. R. Oppenheimer, Ann. Physik, 84, 457, (1927).

nuclear coordinates as parameters, and a part depending only on nuclear coordinates

$$\Psi = \psi_{y_1 \cdots y_N}(X_1, \ldots X_K)\, \phi(y_1, \ldots y_N)$$

We define the part of H_{Ne} depending on electron coordinates and nuclear charges as H_e. Then

$$H_e\, \psi_{y_1 \cdots y_N}(X_1, \ldots X_K) = E_{e, y_1 \cdots y_N}\, \psi_{y_1 \cdots y_N}(X_1 \ldots X_K), \tag{3}$$

where we show the Schrödinger equation for the electrons, from which we obtain the electron energy and state, for a particular arrangement of the nucleii described by the values of the parameters $(y_1, y_2 \ldots y_N)$.

Through application of the adiabatic approximation,[15] where we include the functional dependence of E_e and ψ on the y's, assuming only that the electron motion can adjust at every instant to the changing positions of the nucleii, and with the motion still determined by (3), we obtain

$$\sum_{a=1}^{N} -\frac{\hbar^2}{2M} \nabla_a^{2} \phi + E_e(y_1, y_2 \ldots y_N)\phi = E\phi \tag{4}$$

We see from this development that the internuclear potential E_e [for that is the role it plays in (4)] is a function of the positions of all the nucleii, and results from the presence of the atomic electrons and nuclear charges.

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[15] A complete development of the adiabatic approximation applied to the present problem is given by F. Seitz in Modern Theory of Solids (McGraw Hill Book Co., Inc., New York, 1940) p. 470.

To obtain an explicit form for E_e, detailed study of (4) is required.

Hirschfelder, Curtiss and Bird[16] have described the commonly used phenomenological forms of the interaction potential of He^4 atoms, and have given an overview of the theory. DeBoer[17] has compared several of these forms of the potential. Moore[18] has made a recent contribution to the theory of the repulsive core of the potential.

At distances large compared to the Bohr radius, the interaction of two helium atoms as described by (4) is characterized by the van der Waals interaction, which arises from attraction between the electric dipole moments mutually induced in the electron charge distributions. This interaction energy depends inversely on the sixth power of the separation distance r of the atoms. There are also higher order terms; the next is the dipole-quadrupole energy, which is proportional to r^{-8}. At close distances of approach, of the order of two Bohr radii, the potential is steeply repulsive, roughly proportional to $e^{-4.60r}$ (r in Å). The electron clouds are stabilized around each nucleus and strongly repel each other when they start to overlap because of both Coulomb repulsion and the Pauli principle.

The phenomenological forms of the potential have been obtained by fitting the theoretical forms for the potential to the temperature depend-

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[16] J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, <u>Molecular Theory of Gases and Liquids</u> (Wiley and Sons, New York, 1954) pp. 1064 and 196.

[17] J. DeBoer, Physica <u>24</u>, S 91, (1958).

[18] H. Moore, J. Chem. Phys. <u>33</u>, 471, (1960).

ence of the second virial coefficient of the rare gases in the gaseous state. A form of the potential which has been calculated with low temperature data and which has been found to predict the virial coefficient with good accuracy to at least 1° K is that of Buckingham, Hamilton and Massey,[19] hereafter termed B.H.M. This potential has the form:

$$V(r) = \left[770\, e^{-4.60r} - \frac{1.49}{r^6}\right] \times 10^{-12}\ \text{erg} \qquad r \leq 2.61\ \text{A.}$$

$$V(r) = \left[977\, e^{-4.60r} - \frac{1.50}{r^6} - \frac{2.51}{r^8}\right] \times 10^{-12}\ \text{erg} \qquad r \geq 2.61\ \text{A.} \tag{5}$$

Analytical application of this form would be difficult. However, the two-parameter potential of Lennard-Jones

$$V(r) = 4\,\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{6}$$

with $\epsilon = 10.22°$ K, $\sigma = 2.556$ A, gives a very close fit to the B.H.M. potential. Its behavior in the region of severe repulsion varies from that of the more precise B.H.M. form, but it will be apparent later that this deviation takes place in a region of such high repulsive potential as to leave physical results unaffected.[20]

Three helium atoms in proximity undergo a three-way induced dipole interaction, which follows the relationship[21]

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[19] R. A. Buckingham, J. Hamilton, and H. S. W. Massey, Proc. Roy. Soc. (London) A179, 103, (1941).

[20] It is later demonstrated that the basic physical effect of the repulsive core is to reduce the probability density obtained from the many-body wave function practically to zero. Either form of the potential is equally effective in this regard.

[21] P. Rosen, J. Chem. Phys. 21, 1007, (1953).

$$\frac{E_{abc}}{E_{ab} + E_{bc} + E_{ca}} = 9.8\, e^{-.66(r_{ab} + r_{ac} + r_{bc})},$$

where r_{ab} is the distance between atoms a and b measured in Bohr radii, E_{abc} is the induced triple dipole energy, and E_{ab} is the two-body energy. In cases of interest to us $r_{ab} > 2.3$ A. Then $E_{abc}/(E_{ab} + E_{ac} + E_{bc})$ is of the order of 10^{-3}, and so can be ignored.

Hence we are correct in stating that $E_e(y_1, \ldots y_N)$ is described adequately for our purposes by (6), and the many-body Hamiltonian, written to include all Coulomb and electronic effects is

$$H_m = \sum_{a=1}^{N} -\frac{h^2}{2M} \nabla_a^2 + \frac{1}{2} \sum_{a,b=1}^{N}{}' \; 4\epsilon \left[\left(\frac{\sigma}{r_{ab}} \right)^{12} - \left(\frac{\sigma}{r_{ab}} \right)^{6} \right].$$

This Hamiltonian is valid under the following liberal conditions:

1. Temperature less than about 50° K
2. Density less than that corresponding to a nearest neighbor distance of 2.5 A.

CHAPTER II

THEORIES OF SOLID HELIUM

Zero-Point Motion in Solid Helium

We shall use the many-body Hamiltonian containing the nuclear position coordinates

$$H = \sum_i - \frac{\hbar^2}{2m} \nabla_i^2 + \frac{1}{2} \sum_{ij}{}' V(r_{ij}) \tag{1}$$

with the potential

$$V(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \tag{2}$$

between pairs of helium atoms.

Our purpose is to solve the Schrödinger equation for the ground state of the solid, ψ_0 and to obtain the ground state energy E_0, given by

$$H\,\psi_0(\vec{X}_1, \vec{X}_2 \, . \, . \, . \, \vec{X}_N) = E_0\,\psi_0(\vec{X}_1, \vec{X}_2 \, . \, . \, . \, \vec{X}_N) \tag{3}$$

where $\vec{X}_1$ describes all the relevant coordinates of particle 1, including spin, of any. ψ_0 must have the symmetry required by the statistics. For He^3, which has spin 1/2 and obeys Fermi-Dirac statistics, we require that

$$P\,\psi_0 = (-1)^p\,\psi_0$$

where P is an operator which permutes the indices of the coordinates, and p is the parity of this permutation. The state in (4) is necessarily antisymmetric under interchange of all the coordinates of two particles. He^4 obeys Bose statistics and has a wave function symmetric under interchange of the coordinates of two particles

$$P_{Bose}\,\psi_0 = (+1)^p\,\psi_0 = \psi_0 \,.$$

We can use the ground state to obtain properties of the solid at finite temperature by superimposing phonons, and spin waves, or applying the molecular field theory of paramagnetism.

The potential (2) is characterized by a weak attraction at large r_{ij}, a minimum near 1.122σ, and a strong repulsion inside $r = \sigma$. The two parameters σ and ϵ can be assigned values to give good representations of the potentials between rare gas atoms, and fair approximations of other systems, such as nucleon-nucleon, nitrogen-nitrogen, etc. Hence we can consider a broad class of problems by reducing (1), (2) and (3) to dimensionless form. Following the discussion of Bernardes,[1] we define

$$\begin{aligned} \tilde{X}_i &= \frac{\vec{r}_i}{\sigma}\,, \\ \tilde{E}_0 &= E_0/\epsilon\,, \\ \tilde{r}_{ij} &= r_{ij}/\sigma\,, \qquad\qquad (5) \\ \psi(\tilde{X}) &= \psi(\tilde{X}\,\sigma) = \psi(\vec{r}_i)\,, \end{aligned}$$

and $\qquad \tilde{\nabla}^2 = \sigma^2\,\nabla^2.$

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[1] N. Bernardes, Theory of Solid He^3, Helium Three (Edited by J. Daunt, Ohio State University Press, Columbus, Ohio, 1960) p. 115.

The last relationship is given by $(1/\sigma^2)\,\partial^2/\partial\tilde{X}_i^{\,2}\,[\psi(\tilde{X}_i\sigma)] = \partial^2\,\partial X_i^{\,2}\psi(r_i)$, where the Laplacian is schematically represented by the second partial derivative.

Using the definitions (5), (3) becomes

$$\sum_i -\lambda^2\,\tilde{\nabla}^2\,\tilde{\psi}\,(\tilde{X}_1 \,.\,.\,.\, \tilde{X}_N) + \sum_{i,j} \frac{1}{2}\,\tilde{V}(\tilde{X}_1 \,.\,.\,.\, \tilde{X}_N)\,\tilde{\psi}(\tilde{X}_1 \,.\,.\,.\, \tilde{X}_N)$$

$$= \tilde{E}_0\,\tilde{\psi}(\tilde{X}_1 \,.\,.\,.\, \tilde{X}_N). \qquad (6)$$

where $\lambda^2 = \dfrac{\hbar^2}{2m\,\epsilon\,\sigma^2}$

Equation (6) applies to any physical system described by the two parameter potential (2). The physical properties of a particular system are all contained in the parameter λ and the definition of E_0. Values of λ for various substances are: xenon, 7×10^{-3}; neon, 7×10^{-2}; He^4, 0.347; He^3, 0.302; neutron-proton interaction $\lambda^2 = (20/(V_0 r_0^{\,2}))$, ($r_0$ = nuclear radius in fermis, V_0 = potential depth in Mev, $\lambda \approx 0.3$).

The ideal situation would permit a general form of $\tilde{\psi}$, with λ as a continuous parameter, but no such simplified solution has been obtained for (6).

In the limiting case in which $\lambda^2 << 1$, where the quantum aspects of ψ can be neglected, we obtain

$$\tilde{E}_0 = \sum_{i,j} \frac{1}{2}\,\tilde{V}(\tilde{X}_1 \,.\,.\,.\, \tilde{X}_N),\ \lambda^2 << 1. \qquad (7)$$

In this case, the energy of the ground state is the potential energy lattice sum. The expression (7) is valid for most solids, and

ordinary lattice dynamics, including quantized sound fields, start with (7) and Newton's second law.

For larger λ, the kinetic energy term of (6) (the zero-point energy) is an important part of the energy operator. The theories of liquid helium and nuclear matter have the common central problem of the handling of the kinetic energy term simultaneously with the two-particle potential. Solid He^3 and He^4 share this difficulty.

Theories of Solid Helium Four

Several authors have considered the dynamics of solid He^4. A brief description of their work pertinent to our problem is given here.

(a) Hooton[2] has considered the shape of the potential around the lattice site. The zero-point motion expands the solid so that the nearest interparticle distance lies outside the minimum of the two-particle potential. The resultant lattice sum shows strong anharmonicity. Hooton approximates the resulting well by a harmonic oscillator potential through a variational calculation in the thermodynamic free energy. His results give the thermodynamic properties of a severely anharmonic lattice with large zero point energy. Application of his results in workable form is hindered by the necessity of making Debye-type approximations. Quantum symmetry effects cannot be obtained from his model.

(b) Zucker[3] has also considered the detailed shape of the

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[2]D. J. Hooton, Phil. Mag. 46, 422 (1955); Phil. Mag. 46, 433 (1955); Phil. Mag. 46, 485 (1955).

[3]I. J. Zucker, Proc. Phys. Soc. (London) 73, 965 (1959).

potential well from the lattice sum. He expands the potential about the lattice point (0, 0, 0) as follows:

$$W = W_0 + W_2(x^2 + y^2 + z^2) + W_4(x^4 + y^4 + z^4) + W_6(x^6 + y^6 + z^6),$$

thus ignoring terms like x^2y^2, in order to keep the problem separable. In this expression,

$$W_0 = \frac{1}{2} \sum_r \phi(r)$$

$$W_2 = \frac{1}{2} \sum_r [\phi^{ii}(r) + \frac{2}{r} \phi^{i}(r)]$$

$$W_4 = 1/72 \sum_r [\phi^{iv}(r) + 4/r \, \phi^{iii}(r)]$$

$$W_6 = 1/2160 \sum_r [\phi^{vi}(r) + 6/r \, \phi^{v}(r)]$$

where $\phi(r)$ is the two-particle potential. The problem can be solved as a superposition of three one-dimensional anharmonic oscillators, using W_0, W_2 and W_4.

Zucker obtains an equation of state

$$p = - \left.\frac{\partial W_0}{\partial V}\right)_T - \frac{\partial E_0}{\partial V} ,$$

where E_0 represents the zero-point energy, and is a complicated function of W_2 and W_4. As Zucker points out, his result is unsatisfactory; it is based on an Einstein model and therefore ignores the effects of neighbors other than through the idealized potential. This consideration is in addition to the separability approximation made above.

(c) Dugdale and MacDonald[4] calculate the energy $E(r)$ of a pair

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[4] J. S. Dugdale and D. K. C. MacDonald, Phil. Mag. 45, 811 (1954).

of adjacent atoms separated by a distance (A) in a rare gas solid. They assume a Lennard-Jones type potential energy, with a first-order correction for anharmonicity effects. They further assume that the kinetic energy contribution to the total energy is proportional to the Debye temperature. The Debye temperature is assumed, in turn, to be proportional to $(d^2E/dr^2)^{1/2}$. Using these assumptions, they obtain good predictions of pressure *vs* volume relationships and cohesive energy for the heavy rare gases, and order-of-magnitude results for He^4.

They find that

$$\frac{M\,\Theta^2\,V_0^{2/3}}{E_0} = 1.14 \times 10^3$$

M = molar mass, grams/mole

V_0 = molar volume, cm^3/mole

E_0 = molar energy, cal /mole

$\Theta = \frac{\beta}{2\pi}\ \frac{h}{r}\left(\frac{1}{m}\frac{d^2\,E}{dr^2}\right)^{1/2}$ °K (Debye temperature, β = lattice parameter ≈ unity).

The value 1.14×10^{-3} matches experimental values for Xe, Kr, A, Ne and He^4, with a maximum error of 2%.

The work of Hooton,[2] Fucker,[3] and Dugdale and MacDonald[4] shows clearly that thermal excitations cannot be treated by straight application of the Debye theory of specific heats, and that the lattice specific heat at low temperatures must come from a more fundamental consideration of the dispersion law for sound waves in the solid. Their results include the effect of the zero-point motion, but they do not include a description

of more than one atom in the lattice dynamics (other than through collective motion in sound waves). In other words, they do not include the effect of motions of the neighbors of a particular atom on the potential of that atom that arises from the neighbors.

Theories of Solid Helium Three

The theory of solid He^3 has been considered by Bernardes and Primakoff[5] (hereafter termed B.P.) and by Bernardes.[6]

(a) Bernardes and Primakoff (Heitler-London approach)

In approaching the solution to (1), B.P. used the potential (2), and a variational wave function consisting of a product of Gaussian functions centered at lattice points:

$$\Phi_0 = \prod_j \text{const}\; e^{-\frac{\alpha^2 r_j'}{2}} = \prod_j \phi_j(r_j'). \tag{8}$$

If Φ_0 is used to evaluate the energy expectation value, the singularity in the potential function yields an infinite result. To avoid this difficulty, B.P. modify the potential by a factor which gives the limit zero as r_{ij} goes to zero. Their effective potential is

$$V_{eff}(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] e^{-\frac{c\,\sigma^{10}}{r_{ij}^{10}}} \tag{9}$$

The cut-off factor $\exp(-c\,\sigma^{10}/r_{ij}^{10})$ is chosen for computational convenience. The value of c is estimated by calculating known properties of He^4 using (9), with various values of c, until the best fit is

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[5] N. Bernardes and H. Primakoff, Phys. Rev. 119, 968 (1960).

[6] N. Bernardes, Phys. Rev. 120, 1927 (1960).

obtained. In particular, the cohesive energy and root-mean-square derivation of atoms from lattice sites for He^4 were calculated by a variational calculation using the parameter α. The value of α that gave the most consistent results in these calculations was then assumed to apply equally well to He^3. Using this assumption, they obtain the expectation value of (1) for the He^3 mass:

$$K(V, \alpha) = N \int d^3 \vec{r}\,' \, \phi^*(\vec{r}\,') \left[- \frac{\hbar^2}{2m} \nabla^2 \right] \phi(\vec{r}\,')$$

$$+ \frac{1}{2} \sum_{i \neq j}^{N} \iint d^3 \vec{r}_1^{\,\prime} \, d^3 \vec{r}_2^{\,\prime} \, \phi^*(\vec{r}_1^{\,\prime}) \, \phi^*(\vec{r}_2^{\,\prime})$$

$$\times V_{eff}(|\vec{R}_i - \vec{R}_j - \vec{r}_1^{\,\prime} + \vec{r}_2^{\,\prime}|) \, \phi(\vec{r}_1^{\,\prime}) \, \phi(\vec{r}_2^{\,\prime})$$

$$\equiv N\epsilon \, W_0 + N\epsilon \, U_0 \tag{10}$$

where $\vec{r}_i^{\,\prime}$ is the coordinate of particle i in a frame with $\vec{R}_i$, the position of the lattice point i, as origin, and the integration is performed over all space. The specific volume V enters through $\vec{R}_i - \vec{R}_j$. The assumption has been made that the effect of introducing symmetry into the wave function has a small effect on K and its variations. B.P. use the condition

$$\frac{\partial}{\partial \alpha} K = 0$$

to find K.

Having found a value for α as a function of volume, B.P. form a symmetrized wave function and calculate an exchange energy:

$$J = \iint d^3\vec{r}_1\, d^3\vec{r}_2\, \phi^*(\vec{r}_2 - \vec{R}_{12})\, \phi^*(\vec{r}_1)$$

$$\times \left[-\frac{h^2}{2m}\, (\nabla_1^{\,2} + \nabla_2^{\,2}) + V_{eff}(|\vec{r}_2 - \vec{r}_1|) \right] \phi(\vec{r}_1 - \vec{R}_{12})\, \phi(\vec{r}_2)$$

$$\equiv J_W + J_U \,. \tag{11}$$

Here $\vec{R}_{12}$ is the vector between nearest neighbor lattice points, J_W is the kinetic energy part of the integral, and J_U is the potential energy part.

B.P. find that $J_U = 3.2 \times 10^{-3}\epsilon$ and $J_W = -5.4 \times 10^{-3}\epsilon$, with $J = -2.2 \times 10^{-3}\epsilon = -0.02°$ K.

From their values of E and J, B.P. then proceed to obtain values for specific heat, entropy, susceptibility, and other thermodynamic properties of the solid.

There are no satisfying supporting physical arguments for the effective potential used by B.P., and for their assumption that the observed behavior of He^4 matches that of He^3 (through the constant c in the effective potential factor). The multiplying factor in the potential energy $\exp(\sigma^{10}\, c\, r^{-10})$ is designed to circumvent this difficulty. However, correlation effects outside 2.6A, although important, are not included. Other questions arise which are open to discussion:

(1) The product of single-particle orbitals used by B.P. does not include particle correlations properly. This fault of the single-particle function has been discussed by many authors.[7] The difficulty can be understood by considering

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[7] R. K. Nesbet, Revs. Modern Phys. 33, 28 (1961) discusses the correlation problem and gives many references.

$$\langle V_{12} \rangle = \int \phi_1^*(1)\, \phi_2^*(2)\; V_{12}(r_{12})\, \phi_1(1)\, \phi_2(2) d\tau_1\, d\tau_2 \, . \qquad (12)$$

If the single-particle orbitals have any region of overlap at all, and $V_{12}(r_{12})$ has a singularity stronger than $1/r^2$, then $\langle V_{12} \rangle$ is infinite, contrary to physical actuality. This consideration sheds doubt particularly on the computed exchange integral, which is determined by the behavior of the wave function in regions of overlap.

(2) B.P. performed their calculations assuming a face-centered cubic lattice. They make the conjecture that their numerical values apply at least semiquantitatively to the body-centered cubic configuration. However, since the exchange integral is highly sensitive to particle separation, their calculation of exchange is much less likely to be applicable to both lattice structures at once than their calculation of cohesive energy.

(3) The form of spin-lattice structure in an antiferromagnetic crystal is sensitive to the exchange integral with nearest and next nearest neighbors.[8] In a body-centered cubic lattice, the next nearest neighbors are only 15% farther removed than the nearest neighbors, and the exchange energy with both nearest and next nearest neighbors can be of the same order of magnitude. At temperatures high compared to the Neel temperature, the susceptibility is given by the Curie-Weiss law, $\chi = C/(T + T_C)$. The Curie temperature T_C is given by the energy change in a spin flip, including interactions with all neighbors. (In Chapter V there is further discussion of magnetic effects.)

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[8] J. H. Van Vleck. J. phys. radium 12, 262 (1951).

(b) Bernardes (Non-overlapping Wave Function approach)

Bernardes[9,10] has considered He^3 and He^4 from the point of view of non-overlapping single-particle orbitals. The functions chosen are square-well orbitals, and Bernardes calculates the integral

$$V = \sum_i \sum_j{}' \int \phi_i^*(i)\, \phi_j^*(j)\; V_{ij}(|\vec{r}_i - \vec{r}_j|)\, \phi_i(i)\, \phi_j(j) d\tau_i\, d\tau_j\,, \quad (13)$$

using

$$\phi_i(\xi_i) = \left(\frac{\pi}{2a^3} \right)^{1/2} \frac{\sin(\pi\, \sigma\, \xi_i\, a)}{(\pi\, \sigma\, \xi_i)/(a)} \qquad \xi < a/\sigma$$

$$\phi_i(\xi_i) = 0 \qquad \xi_i \geq a/\sigma \quad (14)$$

He obtains a series in $(a/\pi c)$ for $\langle H \rangle = \langle T \rangle + \langle V \rangle$, and minimizing $\langle H \rangle$, obtains a value for a. The series expansion coefficients are different for body-centered cubic and face-centered cubic lattices. Hence Bernardes can declare one lattice or the other most stable. He finds that both He^3 and He^4 assume closest packing, whereas experimentally He^3 is body-centered cubic, and He^4 is hexagonal close-packed.

The integral (13), although it is finite, still overestimates the potential energy. The true wave function gives a different probability density describing particle "a" for each assumed position of particle "b". The simple product wave function gives a distribution function for particle

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[9] N. Bernardes, Phys. Rev. 112, 1534 (1958).

[10] N. Bernardes, Phys. Rev. 120, 1927 (1960).

"a", in a form showing no dependence on the position of particle "b". This shortcoming prevents an accurate estimate of average potential energy, except in the limit of large separation.

CHAPTER III

A WAVE FUNCTION WITH CORRELATIONS
THE PLUVINAGE METHOD

Meaning of Particle Correlations

An elementary discussion will clarify the meaning of the term "particle correlations."

The usual description of a many-body system in coordinate space is a product of single-particle orbitals (hereafter called S.P.O.),

$$\Phi = \prod_{i=1}^{N} \phi_i(\vec{r}_i). \qquad (1)$$

Here, the form of the ϕ's is determined by the boundary conditions imposed on the system and by the Schrödinger equation.

In (1), we have ignored symmetry requirements. We merely state that correlations resulting from the Pauli exclusion principle are not our concern in this section.[1] The product (1) is the wave function of the Hartree approximation and is the wave function of B.P.[2] (apart from symmetrizations). This type of function can be used to describe exactly the state of N non-interacting particles, and can be used as a variational

[1] To be precise, this product must be constructed to give a definite symmetry under interchange of particle coordinates. The results of this section are unchanged if we include symmetry by writing $\Phi = \sum_P P\, \phi_i(\vec{X}_i)$, where P permutes the indices of $\vec{X}_i$, assigns the proper sign (+ or -) to the permutation, and normalizes the product. The spin variable, if any, is included in X_i. The symbol r_i will be consistently used to represent space coordinates only.

[2] N. Bernardes and H. Primakoff, Phys. Rev. 119, 968 (1960).

starting point for interacting particles. In general, (1) fails for strongly interacting, dense systems.

Lee, Huang, and Yang,[3] in their analysis of strongly-interacting (hard-sphere) particles, use (1) in a particular form:

$$\phi = \sum_{k_1, k_2, k_3 \ldots k_N} C(k_1, k_2, k_3 \ldots k_N)\, U_{k1}(\vec{r}_1)\, U_{k2}(\vec{r}_2) \ldots U_{kN}(\vec{r}_N). \qquad (2)$$

Here the $U_k(\vec{r})$ are a complete orthonormal set of wave functions. The coefficients C carry the symmetry of the wave function. This function can be used to calculate the hard-core problem, if many different combinations of k_i are used. Lee, Huang, and Yang transfer (2) to a representation expressed by occupation numbers in k space. They perform a variational calculation, valid at low densities. In a crystal order the solution in k space must transform to a solution in r space showing crystalline order. This operation has not been successfully performed. Besides failing to demonstrate crystalline order, the theory of Lee, Huang, and Yang is valid for dilute systems only and invalid for systems as dense as the one under consideration here.

To help describe a state showing crystal symmetry we keep the basic description in coordinate space. We use a less drastic separation of Φ than (7) and include a functional dependence on the mutual separation of the particles,

$$\Phi = \prod_{i > j} \phi_{ij}(\vec{r}_i, \vec{r}_j). \qquad (3)$$

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[3] T. D. Lee, K. Huang, and C. N. Yang, Phys. Rev. 106, 1135 (1957).

We study equation (3) by considering in some detail the behavior of two interacting particles in a box.

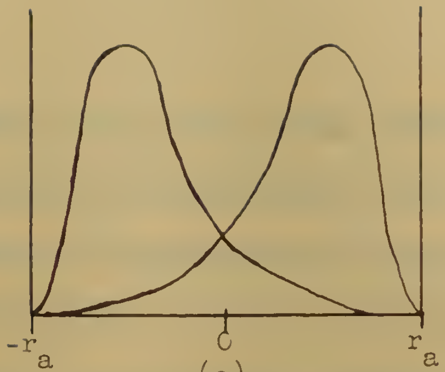
The usual interpretation of the probability density corresponds to a contour map, with the frequency of observation of a particle as the elevation, and the position of the observation as the location on the map. The "map" should, of course, show conditions in a 3-dimensional solid, rather than conditions on a plane.

In Fig. 1(a), we show, in a qualitative presentation, the probability density for two particles contained in a spherical well of infinite potential and radius r_a. The curves show the "elevations" along a line drawn through the "map." The state is represented by $\phi_1(\vec{r}_1)\,\phi_2(\vec{r}_2)$. The configuration is intended to represent the state of lowest energy (ground state) in the S.P.O. approximation obtained, for example, by the Hartree-Fock method. If Fig. 1(a) has validity, it must correspond to weakly interacting particles. We have already seen, in the case of B.P., that, if we calculate a potential energy value using a S.P.O. wave function, difficulty can arise. In the integral

$$\langle V \rangle = \int_{v_1}\int_{v_2} |\phi_1(\vec{r}_1)|^2 |\phi_2(\vec{r}_1 + \vec{r}_{12})|^2 V(|\vec{r}_{12}|)\, d^3\vec{r}_{12}\, d^3\vec{r}_1 \;,$$

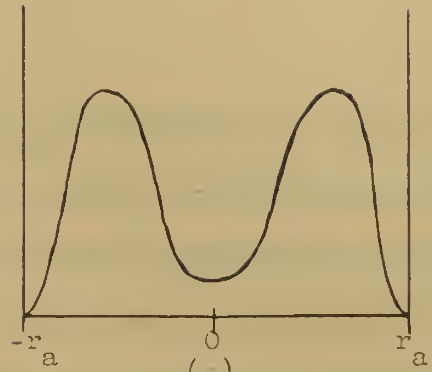
we assume $V = A|\vec{r}_{12}|^{-n}$. For $n > 2$, the integral diverges if ϕ_1 and ϕ_2 overlap anywhere. In the present case there is complete overlap, and $n = 12$, so that Fig 1(a) cannot represent helium atoms.

We next improve the description by retaining a general functional dependence on the positions of both particles, writing $\Phi = \psi(\vec{r}_1, \vec{r}_2) \equiv \psi(1, 2)$. We cannot separate $\psi(1, 2)$ into a product of $\phi_1(\vec{r}_1)\phi_2(\vec{r}_2)$.



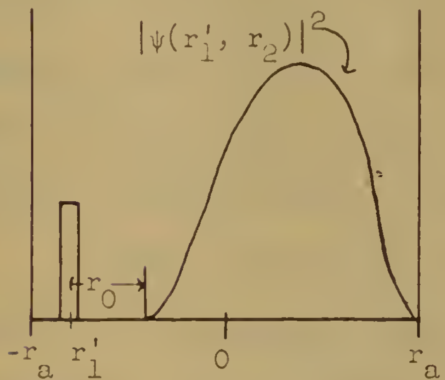
(a)

Two particle density
S.P.O. approximation



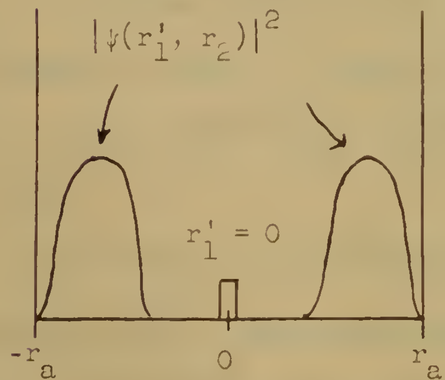
(b)

Correlated single particle
density, f(1')



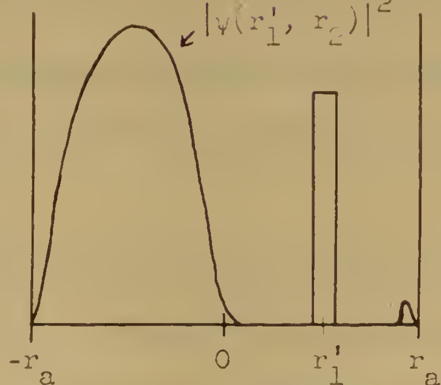
(c)

Correlated two particle
density, particle 1 at r_1'



(d)

Correlated two particle
density, particle 1 at r_1'



(e)

Correlated two particle
density, particle 1 at r_1'

Figure 1. Particle Correlations

In Figs. 1(b), 1(c), 1(d), and 1(e), using this function, we show how the "contour map" concept must be modified. To draw the curves, we must think of a whole series of maps, where each map corresponds to a particular position of one of the particles, and displays a distribution function for the other particle. (We think of the figures representing a system with the exponent $n > 2$, weakly attractive outside $r_{ij} = r_0$.)

In Fig. 1(b), we show the probability of finding particle ((1)) [hereafter labeled simply ((1))], at r_1', [hereafter labeled (1')], regardless of the position of ((2)). We employ the Dirac δ function to locate ((1)) in d^3r_1 at $\vec{r}_1'$, and write $\int|\psi(1, 2)|^2\, \delta(\vec{r}_1 - \vec{r}_1')d^3\vec{r}_1 d^3\vec{r}_2 = \int|\psi(1', 2)|^2 d^3\vec{r}_2 = f(1')$. We plot $f(1')$.

In Figs. 1(c), 1(d), and 1(e), we illustrate the probability distribution of ((2)), when ((1)) is localized at (1'). This distribution is given by $\int|\psi(1, 2)|^2\, \delta(\vec{r}_1 - \vec{r}_1')d^3(\vec{r}_1) = |\psi(1', 2)|^2$. The particle at (1') is shown as a heavy vertical bar of height $f(1')$, to illustrate the relative probability of each of the maps 1(c), 1(d), and 1(e). The diameter chosen as abscissa is the diameter through (1'). Particle ((2)) is distributed with cylindrical symmetry about this diameter. Hence, the normalizations of Figs. 1(c), 1(d), and 1(e) are related in a complicated way.

In constructing the figures we have assumed a strongly repulsive interaction of radius r_0. If the interactions were weak everywhere, the representation 1(a) would introduce a smaller correlation error.

For three and more particles, we proceed in the same fashion, but with a new set of maps for each additional particle. For example, with

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

three particles, Figs. 1(c), 1(d), and 1(e) can represent the configuration of ((1)) and ((2)) for a given position (3') of ((3)). We can write the three-particle function as $\psi(1, 2, 3)$, a three-particle orbital; as $\psi(1, 2)\ \psi(2, 3)\ \psi(1, 3)$, the two-particle approximation; or as $\phi(1)\ \phi(2)\ \phi(3)$, the single-particle approximation. In the spirit of providing an improvement to the S.P.O., and since we will have no three-particle interactions to deal with, our work uses the two-particle approximation

$$\Phi(1, 2, 3) = \psi(1, 2)\ \psi(2, 3)\ \psi(1, 3),$$

or, in general

$$\Phi(1, 2, 3, \ldots N) = \prod_{i > j} \psi(\vec{r}_i, \vec{r}_j).$$

Use of the Interparticle Coordinate to Provide Correlation Effects

The methods previously applied to the ground state of solid He^3, which include a description of the ground state (for example, B.P.), express correlations through a product of single-particle orbitals. As described in Chapter II, such a description fails in the case of a potential with a strong singularity at the origin. Including the interparticle distance in the state function would remove this objection. The two-particle function of Chapter II offers a way of doing this.

Previous work has considered this problem. In parallel calculations of the temperature dependence of the susceptibility liquid He^3,

Price[4] introduced a fixed interparticle distance, and Rice[5] assumed a hard-core repulsion.

Jastrow,[6] Aviles,[7] Iwamoto,[8] and Drachman,[9] have developed a variational method (the Jastrow method) using a trial function $\prod_i \phi_i(\vec{X}_i) \prod_{i>j} f_\epsilon(\vec{r}_i - \vec{r}_j)$.[10] This function resembles the $\prod_{i>j} \psi(\vec{r}, \vec{r})$ of the last section. The Jastrow method includes a series expansion in cluster integrals similar to those used in obtaining the partition function in classical statistical mechanics of dense systems.[11] The cluster method of obtaining the variational parameter ϵ is unsuited to the solid state because it assumes liquid disorder, and therefore the Jastrow method will not serve our needs. However, the method has points of similarity with our method, and we will return to it later.

Brueckner[12] has developed a method for including two-particle interactions correctly to arbitrary order. The theory is a scattering

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[4] P. J. Price, Phys. Rev. 97, 259 (1955).

[5] O. K. Rice, Phys. Rev. 97, 263 (1955).

[6] R. Jastrow, Phys. Rev. 98, 1479 (1955).

[7] J. B. Aviles, Jr., Ann. Phys. 5, 251 (1958).

[8] F. Iwamoto, Prog. Theoret. Phys. (Kyoto) 19, 597 (1958). F. Iwamoto and M. Yamada, Prog. Theoret. Phys. (Kyoto) 17, 543 (1957).

[9] R. J. Drachman, Phys. Rev. 121, 643 (1961).

[10] The author is indebted to Professor Walter Kohn for pointing out the connection between the present work and the approach of 6, 7, 8, 9.

[11] J. E. Mayer and M. G. Mayer, Statistical Mechanics (Wiley and Sons, Inc., New York, 1940) p. 277.

[12] H. A. Bethe, Phys. Rev. 103, 1353 (1956).

theory, and includes an expansion similar to (2). A workable way of applying the Brueckner method to a solid has not been developed. The pseudopotential method[2] shares this disadvantage.

Pluvinage,[13] in studying the atomic spectrum of helium, used the set of coordinates introduced earlier by Hylleraas.[14] Pluvinage added the feature of including the interparticle distance explicitly in the zero-order Hamiltonian. The zero-order wave function is thus a function of the space coordinates of the particles, contains the interparticle distance, and cannot be separated into a product of single-particle functions. It possesses none of the disadvantages ascribed to other methods in the preceding paragraphs.

Using Pluvinage's method, Walsh and Borowitz[15] (hereafter termed W.B.) have considered the energy levels of several atoms and, in general, get better results in zero order than the more complicated first-order calculations usually performed with hydrogenic wave functions. The method can also be applied to our problem, with reasonable expectation of equally good results.

The Pluvinage Method

The Pluvinage method introduces the interparticle distance into the many-body Hamiltonian and wave function, yielding an exact formal

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[13] P. Pluvinage, Ann. Phys. 5, 145 (1950).

[14] E. A. Hylleraas, Zeits. Physik 65, 209 (1930).

[15] P. Walsh and S. Borowitz, Phys. Rev. 115, 1206 (1959); Phys. Rev. 119, 1274 (1960).

expression which includes explicit dependence on all the interparticle distances, as well as the spatial positions of all the particles.

We write the many-body Hamiltonian:

$$H = -\sum_{i=1}^{N} \frac{\hbar^2}{2m} \nabla_i^2 + \frac{1}{2} \sum_{ij}' V_{ij}(r_{ij}) + \sum_i V_i(\vec{r}_i). \tag{4}$$

Here we describe N identical particles of mass m, interacting with the potential $V(r_{ij})$. We have already seen that we can take $V(r_{ij})$ to be the Lennard-Jones potential

$$\begin{aligned} V(r_{ij}) &= 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \\ \epsilon &= 10.22^\circ\ K \\ \sigma &= 2.556\ A \end{aligned} \tag{5}$$

$V(\vec{r}_i)$ is an externally applied potential, the same function of space for all particles.

We will now follow Pluvinage in introducing the interparticle distance into the Hamiltonian.

In any calculation involving n independent variables $(u_1, v_1, w_1, u_2, v_2, w_2, \ldots)$, we can introduce another set of m variables $(x_1, y_1, z_1, x_2, y_2, z_2, \ldots)$, related to the u^i by $x^i = x^i(u^i)$, and possibly simplify the calculation. We can even have $m > n$, provided that we also provide $m - n$ independent constraints in the functions $x^i(u^i)$. In Appendix A we show that the following statement is true:

If $\psi_1(u^i) = \psi_1(u_1, v_1, w_1, u_2, \ldots w_N)$, a function of the Cartesian coordinates (u_i, v_i, w_i) of N particles in a system, we may set up

another function $\psi_2(x^i) = \psi_2(x_1, y_1, z_1 \cdots y_N z_N, r_{12} r_{13} \cdots r_{N-1,N})$, which contains $(N)(N-1)/2$ extra coordinates, and we may require that $\psi_1(u^i) = \psi_2(x^i)$ everywhere in space. In order to do this, we must have $(3N + (N)(N-1)/2)$ independent relations $x^i = x^i(u^i)$, and the rule of differentiation

$$\frac{\partial\psi_1}{\partial u^j} = \frac{\partial\psi_2}{\partial u^j} = \sum_{i=1}^{n} \frac{\partial x^i}{\partial u^j} \frac{\partial\psi_2}{\partial x^i}$$

In our case, the Hamiltonian contains the interparticle distances r_{ij}, so we are led to introduce them as extra coordinates.

We then have

$$\begin{gathered} x_1 = u_1 \quad y_1 = v_1 \quad z_1 = w_1 \\ r_{12} = \sqrt{(u_1 - u_2)^2 + (v_1 - v_2)^2 + (w_1 - w_2)^2} \end{gathered} \tag{6}$$

as the $3N + N(N-1)/2$ independent relations.

In what follows, we shall use a wave function of the type ψ_2, which gives the same results as ψ_1, simply because we require $\psi_1 = \psi_2$. We shall find that ψ_2 yields a useful natural separation.

We drop the distinction between x_1 and u_1, but remember the special role the x's play in the functional form of r_{12}. From Appendix A we have the rule of differentiation:

$$\frac{\partial}{\partial x_i} \rightarrow \frac{\partial}{\partial x_i} + \sum_j \frac{\partial r_{ij}}{\partial x_i} \frac{\partial}{\partial r_{ij}} \tag{7}$$

Here, to the right of the arrow, we speak of a ψ_2 type of description, to the left, ψ_1.

From Appendix A, we have

$$\sum_i \nabla_i^2 \rightarrow \sum_i \nabla_i^2 + \sum_{i,j} \left[\frac{\partial^2}{\partial r_{ij}^2} + \frac{2}{r_{ij}} \frac{\partial}{\partial r_{ij}} \right]$$

$$+ \sum_{i \neq j} \frac{2\, \vec{s}_{ij} \cdot \vec{\nabla}_{s,ij}}{r_{ij}} \frac{\partial}{\partial r_{ij}} + \sum_{i \neq j \neq k} \vec{s}_{ik} \cdot \vec{s}_{ij} \cdot \frac{\partial}{\partial r_{ik}} \frac{\partial}{\partial r_{ij}} \, . \quad (8)$$

Here, we have put

$$\vec{\nabla}_{s,ij} = \frac{\partial}{\partial s_{x,ij}} \hat{i} + \frac{\partial}{\partial s_{y,ij}} \hat{j} + \frac{\partial}{\partial s_{z,ij}} \hat{k} \quad (9)$$

$$s_{x,ij} = (x_j - x_i). \quad (10)$$

Here $\vec{s}_{ij}$ is the vector $\vec{r}_j - \vec{r}_i$. It is used to express relative displacements in terms of the variables $x_i = u_i$, $y_i = v_i$, $z_i = w_i$. The symbol r_{ij} is one of the $N(N - 1)/2$ additional coordinates,

$r_{ij} = \sqrt{(u_j - u_i)^2 + (v_j - v_i)^2 + (w_j - w_i)^2}$. We need both r_{ij} and $\vec{s}_{ij}$ since derivatives in x space, like $\partial/\partial x$ or $\vec{\nabla}_{s,ij}$, operate on functions of x, y, z, and $\vec{s}$ but not on functions of r_{ij}. Likewise, derivatives such as $\partial/\partial r_{ij}$ do not operate on functions of x, but do operate on functions of r_{ij}. In addition to the interparticle vector $\vec{s}_{ij}$, we will also have need of the position of the center of mass of pair ij, expressed in x, y, z space.

$$2\, \vec{t}_{ij} = \vec{r}_j + \vec{r}_i \quad (11)$$

We can write the Hamiltonian H,

$$H = H_0 + H' \quad (12)$$

$$H_0 = \sum_i - \frac{\hbar^2}{2m} \nabla_i^2 + \sum_i V_i(\vec{r}_i) + \sum_{i,j}' \frac{1}{2} V(\vec{r}_{ij}) - \sum_{i,j} \frac{\hbar^2}{2m} \nabla_{r,ij}^2 \qquad (13)$$

$$H' = - \sum_{i,j}' \frac{\hbar^2}{m} \frac{\vec{s}_{ij} \cdot \vec{\nabla}_{s,ij}}{r_{ij}} \frac{\partial}{\partial r_{ij}}$$

$$- \sum_{j \neq k \neq i} \frac{\hbar^2}{2m} \vec{s}_{ij} \cdot \vec{s}_{ik} \frac{\partial^2}{\partial r_{ij} \partial r_{ik}} \qquad (14)$$

In (13), $\nabla_{r,ij}^2 = \dfrac{\partial^2}{\partial r_{ij}^2} + \dfrac{2}{r_{ij}} \dfrac{\partial}{\partial r_{ij}}$.

An attempt to use the total Hamiltonian to determine a set of eigenstates of the Schrodinger equation appears uninviting. Instead, we use an approximation introduced by Pluvinage. We look upon H' as a perturbation, and look for the states of H_0:

$$H_0 \Phi = E_0^{(n)} \Phi \qquad (15)$$

Here Φ is a function of the $3N + N(N-1)/2$ variables ($\vec{r}_1, \vec{r}_2, \ldots \vec{r}_N$; $r_{12}, r_{13}, \ldots r_{23}, r_{24}, \ldots r_{34}, \ldots r_{N-1,N}$). We attack (15) by the standard method of separation of variables; the form of H_0 makes the solution separable as follows:

$$\Phi = \sum_P P \left[\prod_i \phi_i(\vec{r}_i) \, \eta_i(\zeta_i) \right] \left[\prod_{i > j} \chi(r_{ij}) \right] \qquad (16)$$

Here we show the spin function η_i, a function of the spin variable ζ_i. The state function Φ is an approximation to the true-state function. If the perturbation potential H' is truly small, the approximation will give little error in the energy level of the ground state.

$$E = E_0 + \frac{\langle \Phi | H' | \Phi \rangle}{\langle \Phi | \Phi \rangle} \tag{17}$$

In working with the function Φ, we must remember the role of parameters of integration. We must, therefore, follow a program which has the following steps:

(a) Solve (15) for Φ

(b) In using H_0 and H', let $\partial/\partial x$ operate on x, s_x, t_x only, and let $\partial/\partial r_{ij}$ operate on r_{ij} only.

(c) After differentiation [step (b)], introduce the constraint $r_{ij} = [(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{1/2}$.

(d) After introducing the constraint, evaluate matrix elements by integration.

Note that the order of steps (b), (c), and (d) cannot be altered. As in any analysis involving a parameter, we can, however, first introduce the constraint, and then perform any remaining differentiation by ordinary rules of differentiation not involving $\partial/\partial r_{ij}$. We shall find that this latter program will permit the calculation of the average cohesive energy.

Pluvinage and W.B. have shown that (17) yields excellent values of E for several systems they have analyzed. Further, they have succeeded in obtaining good results by considering only E_0, after making additional assumptions concerning the function Ψ.

Removal of the Singular Interparticle Potential

The Hamiltonian (11) still contains the singular interparticle potential. The various applications of the Pluvinage method differ in the handling of the potential $V(r_{ij})$. Here, we show how to use the Pluvinage method with strongly repulsive interactions.

$H_0\Phi$ in (15) contains the following terms depending on r_{ij}:

$$\sum_P P \sum_{i,j} \left[-\frac{\hbar^2}{2m} \nabla^2_{r,ij} + \frac{1}{2} V_{12}(r_{ij}) \right] \prod_{i > j} \chi(r_{ij}) \prod_k \phi_k(\vec{r}_k).$$

We can make this term vanish, and with it, the potential $V_{ij}(r_{ij})$, by requiring[16]

$$\left[-\frac{\hbar^2}{2m} \nabla^2_{r,ij} + \frac{1}{2} V(r_{ij}) \right] \chi(r_{ij}) = 0. \qquad (18)$$

Expression (18) can be looked upon as a mathematical artifice designed to surmount the difficulty of the singular potential. It can also be considered a Schrodinger equation defining a particular member of the continuum of states, the lowest lying of such states, that of zero energy.

In Appendix B we solve (18) by changing from variable r to variable $q = c/r$, taking χ as a power series in ascending positive powers

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[16] We could write the right-hand side of (18) as $\epsilon_{ij} \chi_{ij}(r_{ij})$. We would find no bound states, hence $\epsilon_{ij} \geq 0$. For $\epsilon_{ij} > 0$, there would be oscillations in χ at large distances, which would cause real trouble in describing an extensive solid. Since we hope to have the functional form of $\chi(r_{ij})$ be independent of r_{ij}, we must eliminate oscillations at the outset by having $\epsilon_{ij} = 0$. We could still solve (18) with $\epsilon_{ij}\chi_{ij}$ on the right, and then set $\epsilon = 0$, but this process would only serve to introduce additional terms in the series expansion for χ which would contain ϵ as a multiplier, a needless complication.

of q. The result, for the physical parameters of He^3, is a rapidly converging series. The two linearly independent solutions are

$$\chi_0 = C_0\, F_0(\sigma/r)$$

$$\chi_1 = C_1(\sigma/r)\, F_1(\sigma/r)$$

$$F_0(x) = 1 - \frac{B}{4.3}\, x^4 + B^2/(8 \cdot 7 \cdot 4 \cdot 3)\, x^8 + B/(10 \cdot 9)\, x^{10}$$

$$- B^3/(11 \cdot 12 \cdot 8 \cdot 7 \cdot 4 \cdot 3)\, x^{12} + \ldots$$

$$F_1(x) = 1 - B/(4 \cdot 5)\, x^4 + B^2/(9 \cdot 8 \cdot 5 \cdot 4)\, x^8 + B/(11 \cdot 10)\, x^{10} + \ldots$$

Here $B = m\, \sigma^2 \epsilon\, K\, 4/h^2$, which has the value 16.60 for He^3.

At large r, $\chi_0 \to C_0$, and when $r \to \sigma$ from above, χ_0 tends rapidly to zero. This behavior is characteristic of a hard core interaction. At large r, $\chi_1 = 0$; it then reaches a maximum at an intermediate value of r, and has a finite value at $r = \sigma$. In Appendix B, χ_1 is shown to yield a solution with an outgoing flux at large distances. This is an unsatisfactory characteristic which cannot be permitted in Φ_0. We thus choose $C_1 = 0$.

We now demonstrate that $C_0 = 1$. Since the Hamiltonian does not contain the time, we may choose χ to be real. Since F is real, C_0 must be real.

$$C_0 = C_0^*.$$

At large distances of separation the interaction has no effect on the two-particle wave function. Therefore, the probability density for

particles i and j is independent of r_{ij}, and multiplying the wave function by the square of the correlation amplitude leaves the wave function unchanged. That is,

$$\chi_{ij}^{*}(r_{ij} \to \infty)\, \chi_{ij}(r_{ij} \to \infty) = 1.$$

Therefore, $C_0^{\,2}\, F_0^{\,2}(0) = 1$, or $C_0^{\,2} = 1$. We take the positive root of $C_0^{\,2}$.

If we were to use the WKB approximation to obtain the wave function for $r < \sigma$, we would find that χ would continue to fall off rapidly as

$$\exp\left(- \int_{r=\sigma}^{r=r_1} [V(\sigma - r)2m]^{1/2}\, \hbar^{-1}\, dr \right) \times [V(\sigma - r)2m]^{-1/2} .$$

Hence we are justified in assuming that $\chi(r)$ is vanishingly small inside $r = \sigma$ (provided only that we use caution in calculating derivatives for $r \approx \sigma$). Our representation for χ, the series $F_0(\sigma/r)$, has poor convergence properties for $r < \sigma$. Because of the smallness of $\chi(r)$ for $r < \sigma$, we can cut off $F_0(\sigma/r)$ by writing

$$\chi(r_{ij} = F_0(B, r_{ij})\, \theta(r_{ij} - r_0)) \tag{19}$$

Here $r_0 \lesssim \sigma$ where r_0 cannot be much less than σ, and $\theta(x)$ is the step function $\theta(x) = 1$, $x > 0$; $\theta(x) = 0$, $x < 0$.

In Fig. 2, $\chi(r_{ij})$, $\chi^2(r_{ij})$, and $\chi(r_{ij})\chi'(r_{ij})/r_{ij}$ are plotted for He^3. In Fig. 3 we illustrate the comparison between the series function $F_0^{\,2}$ and two approximate analytical representations. The function

$1 - \frac{r_0}{r} e^{-\gamma(r-r_0)}$ shown in both Figs. 2 and 3 is an extremely close fit. This is the trial function which has been found to give the lowest energy, out of many tried in the Jastrow method.[6]

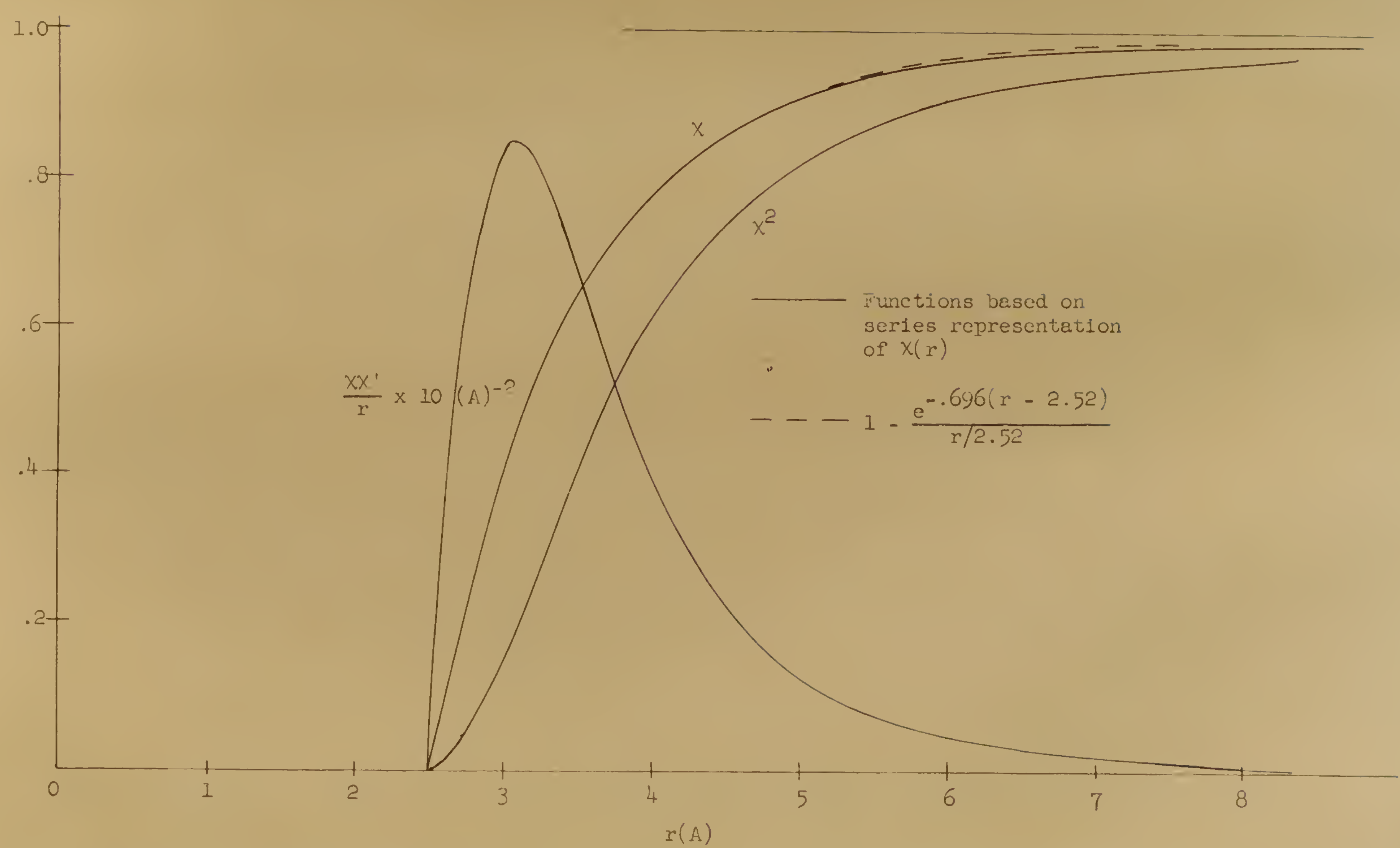

Figure 2. Correlation Amplitude

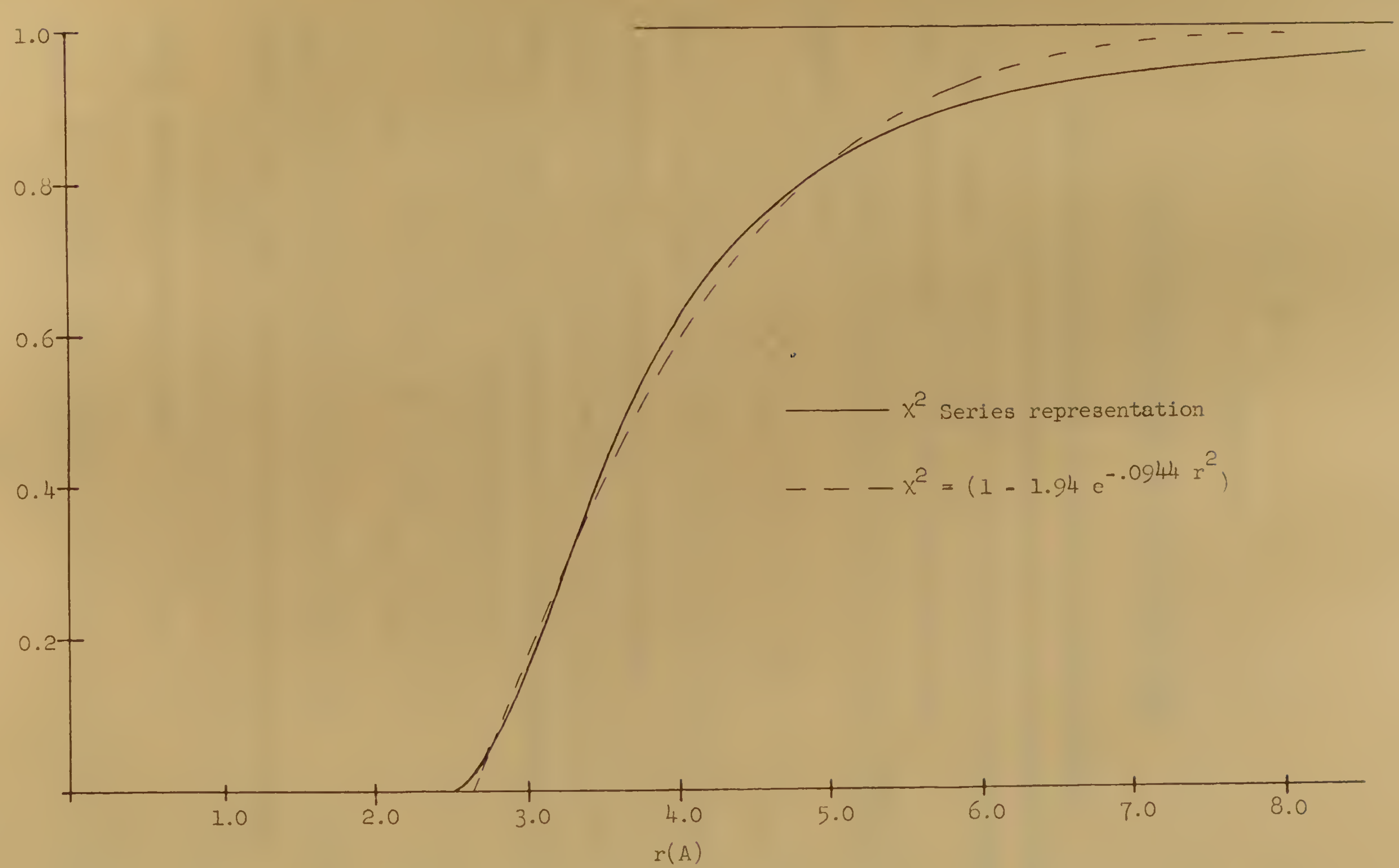

Figure 3. Correlation Probability Density

CHAPTER IV

THE MANY-BODY PROBLEM IN SOLID HELIUM THREE

Density Matrix Formulation of the Many-Body Wave Function

In this chapter we shall develop a theory of the many-body problem which can be applied to dense solids. The development uses the density matrix formalism of Löwdin,[1] which we review briefly here.

We consider the many-body wave function ψ which fulfills the symmetry condition.

$$P\,\psi(\vec{X}_1, \vec{X}_2 \; . \; . \; . \; \vec{X}_N) = (\eta)^p\,\psi(\vec{X}_1, \vec{X}_2 \; . \; . \; . \; \vec{X}_N) \tag{1}$$

where P is a permutation operator working on the subscripts of the coordinates, and p is its parity. For Bose particles, $\eta = 1$. For Fermi particles, $\eta = -1$. The spin variable, if any, is included in $\vec{X}$. A physical quantity Ω associated with the system is represented by a Hermitian operator Ω_{op}. It may be expressed as:

$$\Omega_{op} = \Omega_0 + \sum_i \Omega_i + \frac{1}{2!} \sum_{ij}{}' \Omega_{ij} + \frac{1}{3!} \sum_{ijk}{}' \Omega_{ijk} + \; . \; . \; . \; , \tag{2}$$

where we separate the operator into its zero, one-, two-, . . . particle operators. The prime omits terms having two or more equal indices.

To evaluate the average value of Ω_{op}, we introduce a series of density matrices of various orders:

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[1] P. O. Löwdin, Phys. Rev. 97, 1474 (1955); Phys. Rev. 97, 1490 (1955); Phys. Rev. 97, 1509 (1955).

$$\gamma(\vec{X}_1'|\vec{X}_1) = N\int\psi^*(1'23\ .\ .\ .\ N)\ \psi(123\ .\ .\ .\ N)\ \overline{d\vec{X}_1}\ . \tag{3}$$

The symbol $\overline{d\vec{X}_1}$ signifies integration over all variables except X_1.

$$\Gamma(\vec{X}_1'\ \vec{X}_2'|\vec{X}_1\ \vec{X}_2) = \frac{N(N-1)}{2}\int\psi^*(1'2'3\ .\ .\ .\ N)\ \psi(123\ .\ .\ .\ N)\ \overline{d\vec{X}_1\ d\vec{X}_2}$$

$$\Gamma^{(p)}(\vec{X}_1'\ \vec{X}_2'\ .\ .\ .\ \vec{X}_p'|\vec{X}_1\ \vec{X}_2\ .\ .\ .\ \vec{X}_p) =$$

$$\frac{N!}{p!(N-p)!}\int\psi^*(1'2'\ ...\ p'\ ...\ N)\ \psi(12\ ...\ p\ ...\ N)\overline{(d\vec{X}_1\ ...\ d\vec{X}_p)}$$

$$\Gamma^{(N)}(\vec{X}_1'\ \vec{X}_2'\ .\ .\ .\ \vec{X}_N'|\vec{X}_1\ \vec{X}_2\ .\ .\ .\ \vec{X}_N) = \psi^*(1'2'3'\ ...\ N')\ \psi(123\ ...\ N). \tag{4}$$

The matrices (4) fulfill the following conditions:

$$\Gamma(\vec{X}_1\ \vec{X}_2|\vec{X}_1'\ \vec{X}_2') = \Gamma^*(\vec{X}_1'\ \vec{X}_2'|\vec{X}_1\vec{X}_2)$$

and

$$\Gamma(\vec{X}_2'\ \vec{X}_1'|\vec{X}_1\ \vec{X}_2) = \eta\ \Gamma(\vec{X}_1'\ \vec{X}_2'|\vec{X}_1\ \vec{X}_2).$$

But $\Gamma(\vec{X}_2'\ \vec{X}_1'|\vec{X}_2\ \vec{X}_1) = \Gamma(\vec{X}_1'\ \vec{X}_2'|\vec{X}_1\ \vec{X}_2)$, regardless of η. (5)

We also have

$$\Gamma^{(p-1)}(\vec{X}_1'\ \vec{X}_2'\ .\ .\ .\ \vec{X}_{p-1}'|\vec{X}_1\ \vec{X}_2\ .\ .\ .\ \vec{X}_{p-1})$$

$$= \frac{p}{N+1-p}\int\Gamma^{(p)}(\vec{X}_1'\ \vec{X}_2'\ ...\ \vec{X}_{p-1}'\ \vec{X}_p|\vec{X}_1\ \vec{X}_2\ ...\ \vec{X}_{p-1}\ \vec{X}_p)d\vec{X}_p. \tag{6}$$

The diagonal elements are of special importance

$$\gamma(\vec{X}_1) = \gamma(\vec{X}_1|\vec{X}_1)$$

$$\Gamma(\vec{X}_1,\ \vec{X}_2) = \Gamma(\vec{X}_1\ \vec{X}_2|\vec{X}_1\ \vec{X}_2). \tag{7}$$

These matrices are symmetric for $\eta = \pm 1$. We can interpret $\gamma(\vec{X}_1)dv_1$ as N times the probability of finding a particle in dv_1 at $\vec{r}_1$, with spin ζ_1, regardless of the positions and spins of all the other particles. Similarly, $\Gamma(\vec{X}_1, \vec{X}_2)dv_1\, dv_2$ is the number of pairs, $N(N - 1/2$, times the probability of finding one particle in dv_1 at $\vec{r}_1$ with spin ζ_1 and another in dv_2 at $\vec{r}_2$ with spin ζ_2, regardless of the spins and positions of all other particles. According to (3), we have

$$\int \gamma(1)d\vec{X}_1 = N; \quad \int \Gamma(1, 2)d\vec{X}_1\, d\vec{X}_2 = N(N - 1)/2$$

$$\int \Gamma^p(\vec{X}_1, \vec{X}_2 \; . \; . \; . \; \vec{X}_p)d\vec{X}_1\, d\vec{X}_2 \; . \; . \; . \; d\vec{X}_p = \frac{N}{p!(N - p)!} \tag{8}$$

The matrix $\Gamma^{(p)}$ is antisymmetric in each set of indices when $\eta = -1$. Therefore, if two or more indices are equal, $\Gamma^{(p)} = 0$. In particular

$$\Gamma(\vec{X}_1, \vec{X}_1) = 0, \quad \Gamma^{(3)}(\vec{X}_1, \vec{X}_2, \vec{X}_2) = 0. \tag{9}$$

These relationships are expressions of the Pauli principle.

We now consider the use of operators to obtain average values of physical quantities. Using a two-particle operator as an example,

$$\langle \Omega \rangle = \int \psi^*(\sum_{ij}{}' \Omega_{ij})\psi \; d\vec{X}_1 \; . \; . \; . \; d\vec{X}_N.$$

Evaluating the integral for the general pair 12, we have

$$\langle \Omega \rangle = \tfrac{1}{2} N(N - 1) \int \psi^* \, \Omega_{12} \, \psi \; d\vec{X}_1 \; . \; . \; . \; d\vec{X}_N$$

$$= \binom{N}{2} \int \{\psi^*(1'2'3 \ldots N) \; \Omega_{12} \; \psi(123 \ldots N)\}_{\vec{X}_1'=\vec{X}_1;\; \vec{X}_2'=\vec{X}_2} \; d\vec{X}_1 \; . \; . \; . \; d\vec{X}_N.$$

Applying (3), we get

$$\langle \Omega \rangle = \int (\Omega_{12}\, \Gamma(\vec{X}_1'\, \vec{X}_2' | \vec{X}_1\, \vec{X}_2))_{\vec{X}_1'=\vec{X}_1; \vec{X}_2'=\vec{X}_2}\; d\vec{X}_1\, d\vec{X}_2 \tag{10}$$

We use the convention that Ω_{ij} operates only on the unprimed coordinates $\vec{X}_i$ and $\vec{X}_j$, and not on $\vec{X}_i'$, $\vec{X}_j'$. Hence the non-diagonal elements are needed to express the expectation values of differential operators. Using the convention of (10), we get, for the general operator (2),

$$\begin{aligned} \langle \Omega_{op} \rangle &= \int \psi^* \,\Omega_{op}\, \psi \, d\vec{X}_1 \ldots d\vec{X}_N \\ &= \Omega_0 + \int \Omega_1\, \gamma(\vec{X}_1' | \vec{X}_1) d\vec{X}_1 + \int \Omega_{12} \Gamma(\vec{X}_1'\, \vec{X}_2' | \vec{X}_1\, \vec{X}_2) d\vec{X}_1\, d\vec{X}_2 \\ &\quad + \int \Omega_{123} \Gamma(\vec{X}_1' \vec{X}_2' \vec{X}_3' | \vec{X}_1 \vec{X}_2 \vec{X}_3) d\vec{X}_1\, d\vec{X}_2\, d\vec{X}_3 + \ldots , \end{aligned} \tag{11}$$

In our problem, we have the two-particle operator $V_{ij}(|\vec{r}_i - \vec{r}_j|)$, and do not introduce three-particle operators. Hence, a description of the solid in terms of density matrices of order 2 should give accurage values of $\langle \Omega_{op} \rangle$, as follows:

$$\langle \Omega_{op} \rangle = \frac{\int \left(\Omega_0 + N\, \Omega_1 + \binom{N}{2} \Omega_{12}\right) \Gamma(\vec{X}_1'\, \vec{X}_2' | \vec{X}_1\, \vec{X}_2) d\vec{X}_1\, d\vec{X}_2}{\int \Gamma(\vec{X}_1, \vec{X}_2) d\vec{X}_1\, d\vec{X}_2} \tag{12}$$

In (12), we take care of normalization by the denominator, which is constructed to give unity for $\Omega_{op} = 1$.

Single-Particle Density

(a) In this section, we use the formalism of the density matrices introduced in the preceding section to build up an N particle description of the solid. This description will be approximate, in that it will

describe the properties of the solid in the single-particle sense, just as the Slater determinant describes weakly interacting systems. Our description takes the correlations explicitly into account, an additional refinement not included in the Slater description.

(b) Single-Particle Probability Density. We shall write down the N-body density matrix in terms of the full Pluvinage wave function, and reduce it to a single-particle density matrix. We then show, for dense systems, that a simple representation can be used as the solution to an integral equation, yielding an explicit form for the single-particle density matrix, which includes correlation effects.

The N-body density matrix is

$$\Gamma^{(N)} = \Big|\sum_P P \prod_i \phi_i(\vec{X}_i) \prod_{j>k} \chi(r_{jk})\Big|^2 \qquad (13)$$

In (13), we show the diagonal form and do not introduce prime coordinates. The result is sufficiently general for our needs, since we do not seek expectation values of differential operators, but merely the probability density. Non-diagonal complications will concern us in later sections. When we use (13), we must remember the set of constraints $r_{ij} = +\sqrt{\vec{s}_{ij}\cdot\vec{s}_{ij}}$. It is not necessary to specify the form of χ until we attempt to make numerical calculations. We shall assume, however, that χ is a universal function of the distance between any two particles, independent of the spin of the particles.

From Eq. (3) the single-particle density matrix $\gamma(\vec{X}_1)$ can be obtained by integrating the N-particle matrix over all coordinates except $\vec{X}_1$.

$$\gamma(X_1) = (\text{const}) \int \Gamma^{(N)}(\vec{X}_1 \ldots \vec{X}_i \ldots \vec{X}_N) \overline{d\vec{X}_i} \tag{14}$$

The constant is a normalizing constant depending only on the number of particles. In the first section of this chapter, we evaluated it as N itself.

We can rewrite (14) in terms of the representation (13):

$$\gamma(1) = (\text{const}) \sum_P P_S \phi_1^*(1)\, \phi_1(1) \int \phi_2^*(2)\, \phi_2(2) \ldots \phi_N^*(N)\, \phi_N(N)$$

$$\chi_{23}^2(r_{23}\; \chi_{24}^2(r_{24}) \; . \; . \; . \; \chi_{12}^2 \, d\vec{X}_2 \; \chi_{13}^2 \, d\vec{X}_3 \; \chi_{14}^2 \, d\vec{X}_4 \; . \; . \; . \; . \tag{15}$$

In (15), we have explicitly shown the diagonal form of the density matrix. The permutations refer to interchanging the coordinates of the ϕ_i for both ϕ_i^* and ϕ_i simultaneously. The resulting function is symmetric in the interchange of any two particles. The symbol P_S (S for symmetric) shows this symmetry. The last relationship in (5) shows this property.

An assumption is implied in writing (15) in this way in that we are neglecting the spins of the particles. We have assumed that if

$$\Gamma^{(2)}(1'2'|12) = \begin{vmatrix} \phi_a^*(1') & \phi_a^*(2') \\ \phi_b^*(1') & \phi_b^*(2') \end{vmatrix} \times \begin{vmatrix} \phi_a(1) & \phi_b(1) \\ \phi_a(2) & \phi_b(2) \end{vmatrix},$$

then

$$\Gamma^{(2)}(12|12) = |\phi_a(1)|^2 \; |\phi_b(2)|^2 + |\phi_a(2)|^2 \; |\phi_b(1)|^2. \tag{16}$$

By so doing, we have dropped from $\Gamma^{(2)}(12|12)$ an overlap term $-\,[(\phi_a^*(1)\; \phi_a(2)\; \phi_b^*(2)\; \phi_b(1)) + (\text{complex conjugate})]$. This term contributes positive or negative amounts to $\Gamma^{(2)}$, depending on the relative spin

functions of ϕ_a and ϕ_b. We shall find that (a) correlations keep our particles well separated, and (b) the ϕ's are orthogonal for particles well separated, so that contributions of overlap are very small compared to terms like $|\phi_i(i)|^2$. Hence we are justified in dropping the overlap term when it appears in (15). We will find that we cannot drop this term when we consider exchange effects.

We shall assume throughout that the symmetric permutation of diagonal elements shown in (16) is adequate to describe probability density effects. We shall find later that exchange effects are negligible, thus justifying the assumption.

Writing (15) in modified form, we have

$$\gamma(1) = (\text{const}) \sum_j \phi_j^2(1) \int \{\sum_P P_S\, \phi_2^2(2) \ldots \phi_1^2(j) \ldots \phi_N^2(N)$$

$$\chi_{23}^2 \ldots \chi_{N-1N}^2\} \prod_{k\neq 1} \chi_{1k}\, d\vec{X}_k \, .$$

The term in curly brackets is $\Gamma^{(N-1)}(j, 2, \ldots j-1, j+1, \ldots N)$. Because the diagonal form of Γ is symmetric on interchange of its coordinates, the ordering of the labels is immaterial in the ϕ's as well as the χ's. Hence, in each member of the sum over j, the multiple integrals are identical in form, independent of the position of the index j. We can, therefore, factor out the integral in each sum over j:

$$\gamma(1) = (\text{const}) \left(\sum_j \phi_j^2(1) \right) \int \Gamma^{(N-1)}(j, 2, \ldots N) \prod_{k\neq 1} \chi_{1k}\, d\vec{X}_k . \quad (17)$$

We must now consider the central assumption of this development. We assume that we can project out a single-particle description from the

many-particle description (13), or that there exists a $\gamma(1)$ which describes the average behavior of the solid by assigning certain properties to a single average particle labeled (1). The refinement that we build into $\gamma(1)$ should include the effect of correlations between the particle with coordinate r_1 and the average position of all the other particles, but will not include correlations within other pairs. (These other pairs would enter into a two-body density matrix description $\Gamma(1, 2)$, which describes (a), correlations of 1 and 2 with the average positions of all the other particles, and (b), the actual correlation between 1 and 2.)

The $\chi_{1k}^2(r_{1k})$ in (17) carry the correlation effect between atom 1 and the other atoms k, but we need to know the average positions of the other atoms. For this purpose, expressing $\Gamma^{(N-1)}$ as a product of single-particle density matrices is adequate.

Therefore, if we set

$$\Gamma^{(N)}(1, 2, 3 \ldots N) = \frac{1}{N^N} \prod_{j=1}^{N} \gamma(j),$$

we have an expression which satisfies the relations (3), (4) and (5) applying to density matrices, and specifies the positions of the particles adequately for the purpose of evaluating the integral in (17).

We can now write for (17)

$$\begin{aligned} \gamma(1) &= \text{const} \sum_j \phi_j^2(1) \int \prod_{t\neq 1} \gamma(t) \prod_{k\neq 1} \chi_{1k}^2(r_{1k})\, d\vec{X}_k \\ &= \text{const} \left[\sum_j \phi_j^2(1)\right] \prod_{k\neq 1} \int \gamma(k)\, \chi_{1k}^2\, d\vec{X}_k \end{aligned} \qquad (18)$$

Equation (18) is an integral equation in $\gamma(j)$ which gives the projection of a single-particle state from the many-body state. To obtain it, we have assumed:

(1) The two-particle separation of the wave function, (13), is an adequate description of the N body system;

(2) Among the single-particle states, overlap has a negligible effect on single-particle properties, in that integrals of the type $\int \phi_j(1)\,\phi_k(1)dv_1$, $k \neq j$ all vanish;

(3) $\chi_{ij}(r_{ij})$ is a universal function of the distance r_{ij}, regardless of the identity of i and j.

We have not assumed boundary conditions for the ϕ's, nor a specific functional form for $\chi_{ij}(r_{ij})$.

In the next section, we shall use (18) to obtain an explicit single-particle representation for solid He^3.

A Solution of the Density Equation for Dense Solids

It seems obvious that $\gamma(\vec{r}_j)$ in (14) is a function which has a maximum in its spatial dependence at lattice points and shows the translational symmetry of the lattice. In fact, we can define a solid by requiring that it be described by a $\gamma(\vec{r}_j)$ with these properties. We make the additional assumptions that to a good order of approximation $\gamma(\vec{r}_j)$ has spherical symmetry in its behavior in the immediate neighborhood of lattice points (this consideration is independent of the fact that the maxima of the $\gamma(\vec{r}_j)$ are disposed according to lattice symmetry), that $\gamma(\vec{r}_j)$ decreases monotonically away from lattice sites, and that it is continuous with continuous derivatives everywhere. A simple function with these properties is

$$\sum_j e^{-\delta^2(\vec{R}_j-\vec{r}_i)^2} .$$

Here $\vec{R}_j$ is the position of the lattice site j, and $\vec{r}_i$ is the position of particle i.

We can define a quantity $\gamma_j(\vec{r}_i)$, which is a component of $\gamma(r_i)$

$$\gamma_j(\vec{r}_i) = e^{-\delta^2(\vec{R}_j-\vec{r}_i)^2}\left(\sqrt{\frac{\pi}{\delta^2}}\right)^3$$

$$\gamma(\vec{r}_i) = \sum_j \gamma_j(\vec{r}_i) \tag{19}$$

We must remember that $\gamma(\vec{r}_i)$ has meaning only near lattice sites, which means that large values of $\delta^2(\vec{R}_j - \vec{r}_i)$ give $\gamma_j(\vec{r}_i) = 0$. Hence, (19) presents no complication from overlap, since we have $\delta^2 >> \frac{1}{a^2}$, and the only term of γ that contributes near $\vec{R}_k$ is γ_k.

We redefine terms in (18):

$$\gamma_1(1) = \sum_i |\phi_i(1)|^2 \prod_{j\neq 1} f_j(u_{1j}). \tag{20}$$

The subscript 1 appears on $\gamma_1(1)$ since (20) only describes the density near $\vec{R}_1$. In (20), u_{1j} is the distance $|\vec{R}_j - \vec{r}_1|$ from the field point $\vec{r}_1$ to the lattice site j, and

$$f_j(u_{kj}) = \int \gamma(\vec{r}_j)\,[\chi^2_{kj}(r_{kj})]d\vec{r}_j . \tag{21}$$

Putting the assumed solution (19) into (21), we have

$$f_j(u_{kj}) = (\text{const}) \int \sum_t e^{-\delta^2(\vec{R}_t-\vec{r}_j)^2}\,\chi^2(r_{kj})d\vec{r}_j .$$

Noting that with $\delta^2 >> \frac{1}{e^2}$, all the elements of the sum over t are very small except for $t = j$, we get

$$f_j(u_{kj}) = (\text{const}) \int e^{-\delta^2 q_j^2} \chi^2(r_{kj}) d\vec{r}_j \, , \tag{22}$$

where $\vec{q}_j = \vec{R}_j - \vec{r}_j$, a coordinate with origin at the lattice site j.

When we write (22) in its diagonal form, where we consider only $\gamma_j(j)$, we also obtain only the part of $\gamma(1)$ which describes its probability density around $\vec{R}_1$ and we must obtain the rest of $\gamma(1)$ merely by adding other terms with $e^{-\delta^2(\vec{R}_k - \vec{r}_1)^2}$, $k \neq 1$.

Formula (C-3) of Appendix C tells us that (22) is

$$f_j(u_{kj}) = \chi^2(u_{kj}) + O\left(\frac{\chi \, \chi'}{\delta^2 \, u} \, , \frac{\chi^2}{\delta u} \; e^{-\delta^2(u - r_0)^2} \right) \tag{23}$$

In Appendix C we show that any function χ^2 in the integral (22), which is slowly varying near $r_{kj} = u_{kj}$ compared to $e^{-\delta^2 q_j^2}$ near $q = 0$, will give a result in the form (23). With (23) we can form the product of correlation functions in (20). The result of the product is displayed in formulas (30) and (31), which we now proceed to derive.

Since f_j is well behaved for $u > 2.5$ Å, we can expand $f_j(u_{kj})$ about the value $u_{kj} = R_\lambda$. (Later, R_λ is to be a distance to a shell of atoms equidistent from an arbitrary lattice point as origin.) The expansion is

$$f_j(u_{kj}) = f(R_\lambda) + \Delta_j \, f'(R_\lambda) + \frac{1}{2} \, \Delta^2_j \, f''(R_\lambda) + \ldots$$

where $\Delta_j = |\vec{u}_{kj}| - |\vec{R}_\lambda|$. Denoting $f(R_\lambda)$ by f and $f'(R_\lambda)$ by f', we have

$$f_j(u_{kj}) = f(R_\lambda)\left[1 + \Delta_j \frac{f'}{f} + \frac{\Delta_j^2}{2} \frac{f''}{f} + \ldots\right]. \qquad (24)$$

We define the product $\prod_j f_j(u_{tj}) = F_t$, so that

$$r_1(1) = \sum_i \phi_i^*(1)\,\phi_i(1)\,F_1 . \qquad (25)$$

We have

$$F_k = \left[\prod_t f(R_{\lambda t})\right] \prod_j \left[1 + \Delta_j \frac{f'}{f} + \frac{\Delta_j^2}{2} \frac{f''}{f} + \ldots\right].$$

We introduce a quantity G_k where

$$F_k = \left[\prod_t f(R_{\lambda t})\right] e^{G_k} \qquad (26)$$

G_k is defined as follows:

$$G_k = \ln \prod_j \left[1 + \Delta_j \frac{f'}{f} + \frac{\Delta_j^2}{2} \frac{f''}{f} + \ldots\right]$$

$$= \sum_j \ln \left[1 + \Delta_j \frac{f'}{f} + \frac{\Delta_j^2}{2} \frac{f''}{f} + \ldots\right].$$

But $\ln(1 + x) = x - x^2/2 + x^3/3 - x^4/4 + \ldots$, so that G_k becomes

$$G_k = \sum_j \Delta_j(f'/f) + (\Delta_j^2/2)(f''/f) - (\Delta_j^2/2)(f')^2/(f)^2 + \ldots .$$

But $(d/du)(f'/f) = [f f'' - (f')^2]/f^2$, so we can write

$$G_k = \sum_j G_{k,j} = \sum_j \Delta_j(f'/f)_{R_\lambda} + (\Delta_j^2/2)(d/du\,[f'/f])_{R_\lambda} + \ldots . \qquad (27)$$

We partially imposed the constraint on r_{1j} in evaluating (23). We now complete the process by evaluating G_k for $\vec{r}_k = \vec{r}_1$, the position of particle 1, remembering that $f_j(u_{kj})$ is a function of the distance from lattice site j. The evaluation of G_k proceeds by performing the sum $\sum_j \Delta_j$ and $\sum_j \Delta^2_j$ for constant R_λ, corresponding to a shell of atoms at constant radius, and adding over shells.

Now $\sum_j \Delta_j = \sum_j (|u_j| - |R_{1j}|) = \sum_j (\sqrt{R_{1j}^2 + q_1^2 - 2q_1 R_{1j} \cos\theta} - R_{1j})$. [Figure (4) shows the relationship between u, q and R.] Expanding, we get $\sum_j \Delta_j = \sum_j \{R_{1j}[1 + q_1^2/(2R_{1j}^2) - q_1 \cos\theta/R_{1j} - 4q_1^2 \cos^2\theta/(8R_{1j}^2) + \ldots] - R_{1j}\}$. The sum over $\cos\theta$ yields precisely zero in a Bravais lattice, and in a hexagonal close-packed lattice is zero in the spherically symmetric approximation. We take the average value of $\cos^2\theta$ to be 1/3, getting

$$\sum_j \;_j = \sum_j \frac{q_1^2}{2R_{1j}}(1 - \cos^2\theta) + \ldots = \sum_j \frac{q_1^2}{3R_{1j}} + O(q_1^4).$$

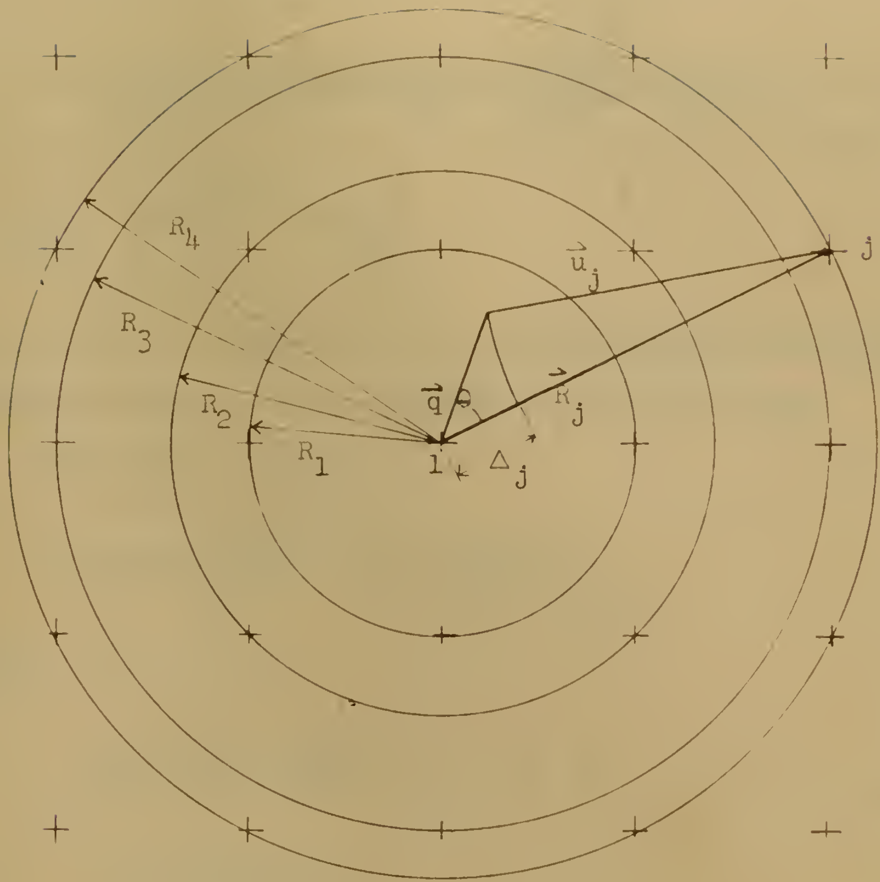
Putting all members of the sum with the same R_{1j} together, we have

$$\sum_j \Delta_j = \sum_\lambda \frac{n_\lambda q_1^2}{3R_\lambda}, \tag{28}$$

where there are n_λ members in the shell at distance R_λ [see Fig. (4)].

Similarly,

$$\sum_j \Delta^2_j = \sum_j \{R_{1j}^2 + q_1^2 - 2q_1 R_{1j}\cos\theta + R_{1j}^2$$
$$- 2R_{1j}^2(1 + \frac{q_1^2}{2R_{1j}^2} - \frac{q_1}{R_{1j}}\cos\theta - \frac{4q_1^2}{8R_{1j}^2}\cos^2\theta + \ldots)\}$$



λ	n_λ	R_λ
1	4	1
2	4	1.414
3	4	2
4	8	2.22

$$\sum_j f(R_j) = \sum_\lambda n_\lambda f(R_\lambda)$$

Figure 4. Lattice Sum for Two-Dimensional Square Lattice

$$= \sum_j q_1^{\,2} \cos^2 \theta + O(q_1^{\,4}) = \sum_j \frac{q_1^{\,2}}{3} + O(q_1^{\,4})$$

$$\sum_j \Delta_{1j}^2 = \sum_\lambda \frac{n_\lambda q_1^{\,2}}{3} + O(q_1^{\,4}) \qquad (29)$$

We did not have to assume a Bravais lattice or spherical symmetry to eliminate the term in $\cos\theta$ leading to the result (29).

We now have from (27)

$$G_1 = \sum_\lambda \frac{n_\lambda q_1^{\,2}}{3} \left[\frac{1}{u} + \frac{1}{2}\frac{d}{du}\right]\frac{f'}{f}\Bigg]_{R_\lambda} .$$

We define

$$g_\lambda = \left[\frac{1}{u} + \frac{1}{2}\frac{d}{du}\right]\frac{f'}{f}\Bigg]_{R_\lambda} , \qquad (30)$$

$$G_1 = \sum_\lambda \frac{n_\lambda}{3} q_1^{\,2} g_\lambda .$$

Now, using (25) and (26),

$$\begin{aligned} \gamma_1(1) &= \sum_i \phi_i^*(1)\, \phi_i(1)\, F_1 \\ &= \sum_i \phi_i^*(1)\, \phi_i(1) \prod_\lambda f(R_\lambda)^{n_\lambda}\, e^{G_1} \\ &= \sum_i \phi_i^*(1)\, \phi_i(1) \left(\prod_\lambda f(R_\lambda)^{n_\lambda}\right) e^{\sum_\lambda \frac{n_\lambda}{3} g_\lambda q_1^{\,2}} . \end{aligned} \qquad (31)$$

The manipulations of formulas (24) to (31) have given us an expression for the probability density of an atom, determined by correlations with all the other atoms of the solid. This important result is the projection in ordinary three-dimensional space of the probability density described in the space with $3N + N(N-1)/2$ variables.

We now put (18) in a form involving δ, the parameter of the Gaussian representation for γ. We have $\gamma_1(1) = e^{-\delta^2 q_1^2}(\pi/\delta^2)^{3/2}$, by hypothesis. Hence,

$$\gamma_1(1)(\pi/\delta^2)^{3/2} = e^{-\delta^2 q_1^2}$$
$$= A \sum_i |\phi_i(1)|^2 \, e^{\sum_\lambda \frac{n_\lambda}{3} \epsilon_\lambda q_1^2} \quad . \tag{32}$$

Here, A is a normalizing factor.

Taking the logarithm, we have

$$\delta^2 = -\sum_\lambda \frac{n_\lambda}{3} \epsilon_\lambda - \frac{\ln A \sum_i |\phi_i(1)|^2}{q_1^2} \, . \tag{33}$$

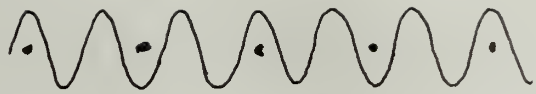
Our assumption that $\gamma_1(1) \propto e^{-\delta^2 q_1^2}$ evidently depends on the relation

$$\lim_{\vec{r}_1 \to \vec{R}_1} A \sum_i \phi_i^2(\vec{r}_1) = e^{-c^2 q_1^2} \, . \tag{34}$$

To work with (34), we must consider the ϕ's in more detail. We assume that they fit the symmetry of the lattice. For example, in a simple cubic lattice, they would have the form

$$\cos\left(\frac{\pi x}{n_i a} + \beta_{n_i}\right) \cos\left(\frac{\pi y}{n_j a} + \beta_{n_j}\right) \cos\left(\frac{\pi z}{n_k a} + \beta_{n_k}\right) ,$$

where $n = N + 1, N, N - 1, \ldots 6, 5, 4, 3, 2, 1, 1/2, 1/3, 1/4, \ldots 1/N - 1, 1/N, 1/N + 1, \ldots$ and the β_{n_i} are phase factors which place the waves in the lattice, so that lattice sites are at the maxima for odd n and $1/n$ and so that the maxima for even n or $1/n$ are midway between atoms. Thus, we have



$n = 1/3$

$n = 1/2$

$n = 1$

$n = 2$

$n = 3$

Evidently the waves with $n < 1$ can be used to construct a packet showing the probability density near individual lattice sites. The long waves, with $n > 1$, do not enter into such packets, but appear when we consider several particles together. For example, we can see from the diagram that if we consider 4 atoms in a row, we must deal with $n = 1$, $n = 2$, $n = 3$, and $n = 4$. Longer wavelengths will not enter.

In performing the integral (22), we could just as well integrate over k and evaluate the correlation with j, as perform the integral over $d\vec{r}_j$. This consideration, together with our formation of the product $\prod_j f_j(u_{1j})$, leads us to the following interpretation of $\prod_k \int \gamma(k)\chi^2_{1k} d\vec{x}_k$: It forms a packet of waves, with wavelengths shorter than about $1/\delta^2$, near $\vec{R}_1$. Therefore, the remaining ϕ_1, which appear explicitly, are determined by other considerations than correlations. For example, they

could be called upon to permit constructing states conforming to the Pauli principle, or to make up eigenstates of parity.

Lowdin,[1] in the third paper of his series on many-particle systems, describes the use of two such states, those for $n = 1$ and $n = 1/2$, as a symmetrized trial function for considering pair interactions in a system such as ours.

In Appendix H, we evaluate the sum $\sum_i \phi_i^2(\vec{r}_1)$ in the somewhat arbitrary case of the central atom $(\vec{R}_1 = 0)$ in a cube of atoms with an odd number of atoms along each edge, requiring symmetry about $\vec{R}_1$. In this case, n_i can assume only odd values and all the θ_n are zero. We assume that the Pauli principle permits two particles in each of the $N/2$ states $n_i = 1, 3, \ldots (N)^{1/3}$. We take the long wavelength component of ϕ_i to be

$$\phi_i(r) \rightarrow C_{ijk} \cos\left(\frac{\pi x}{n_i a}\right) \cos\left(\frac{\pi y}{n_j a}\right) \cos\left(\frac{\pi z}{n_k a}\right) . \quad n = 1,3,5 \ldots (N)^{1/3}$$

We find that $A = 1/(\sum_{ijk} C_{ijk}^2)$, and that all N of the C_{ijk} are equal to the same quantity $C_0 = [8_0{}^3 e/((2\pi)^{3/2} N \,\beta(a))]^{1/2}$. In this expression for C_0, $\beta(a)$ is the value of the correlation product $\prod_k X(R_{1k})$, where R_{1k} is the distance from lattice site 1 to lattice site k. The values of the C's do not enter into (34), however, and the n_i in the denominators of the arguments of the cosines give the convenient result:

$$e^{-\alpha^2 q^2} = e^{-\frac{\pi^4 q^2}{8N^{1/3} a^2}} . \qquad (35)$$

We then have, for S^2,

$$S^2 = S_0^{\ 2} + \sigma^2 ,$$

$$S_0^{\ 2} = -\sum_\lambda \frac{n_\lambda G_\lambda}{3} , \tag{36}$$

where σ^2 is a term of order $N^{-1/3}$, hence negligible for large systems.

In Appendix D, we derive expressions for G_λ. We find that G_λ has two parts. The first part, $G_{\lambda 0}$, is independent of S^2, and another part, $G_{\lambda 1}$, depends on S^2, but is a small correction to G_λ. In the same appendix, we show two expressions for $G_{\lambda 0}$. The first form is

$$G_{\lambda 0,1} = -\frac{B\,\sigma^4}{R_\lambda^{\ 4}}\left[1 + \frac{B\,\sigma^4}{9R_\lambda^{\ 4}} - \frac{\sigma^6}{R_\lambda^{\ 6}} + \frac{B^2\,\sigma^8}{R_\lambda^{\ 8}}\,\frac{2}{189} + 0\left(\frac{\sigma_{10}}{R_\lambda^{\ 10}}\right)\right] , \tag{37}$$

where $\quad B = \dfrac{4m\,k\,\epsilon\,\sigma^2}{\hbar^2}$. $B = 16.60$ for He^3. We obtain (37) by applying (30) to $f'/f = (X^2)'/X^2$, where X is in the series representation. The second form is

$$G_{\lambda 0,2} = \frac{1 - X(R_\lambda)}{R_\lambda^{\ 2}\,X(R_\lambda)}\left[\frac{(1 + \gamma\,R_\lambda)^2}{X(R_\lambda)} - (1 + 2\gamma\,R_\lambda)\right] , \tag{38}$$

where we use the representation $X = 1 - (r_0/r)e^{-\gamma(r-r_0)}$, $\gamma = 0.696$, and $r_0 = 2.52$, for He^3. Note that $G_{\lambda 0}$ is independent of the lattice symmetry. We have shown (37) and (38) in Figure 5.

The part of G_λ which depends on S is

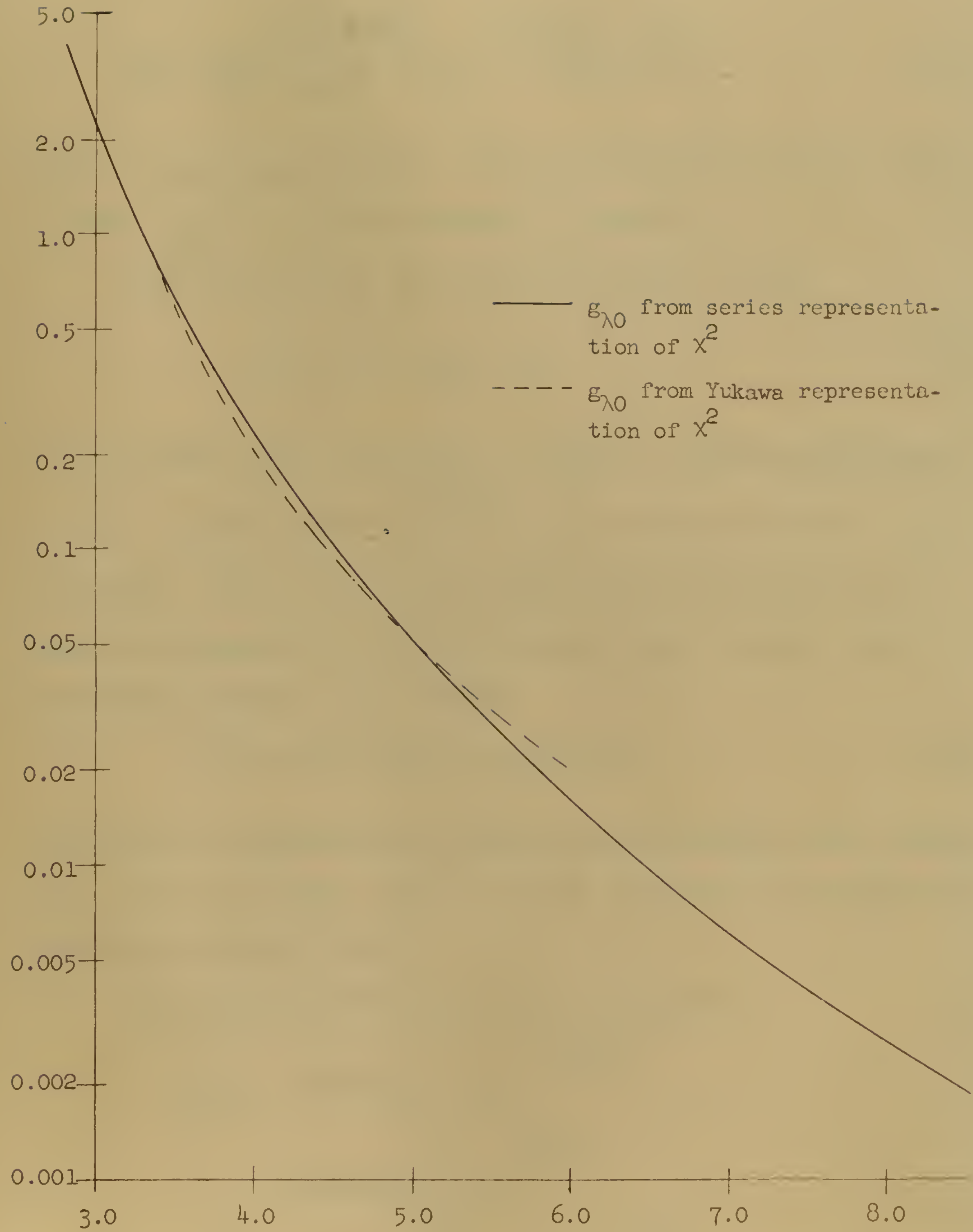


Figure 5. Elements of the Logarithmic Sum, $g_{\lambda 0}$, Plotted Against Radial Distance.

$$g_{\lambda 1} = \frac{-e^{-\delta^2(R_\lambda - r_0)^2}}{\sqrt{\pi}[1 + \phi(\delta[R_\lambda - r_0])]} \left\{ \frac{\delta^3 r_0 (R_\lambda - r_0)}{2 R_\lambda} \right\} \tag{39}$$

where ϕ is the error integral. There are additional negligible terms of order $(g_{\lambda 1})^2$, which are discussed in Appendix D.

From (35), (37) and (39), we can calculate $\delta^2 \approx \delta_0^{\ 2}$

$$\delta_0^{\ 2} = \sum_\lambda \frac{n_\lambda}{3} (g_{\lambda 0} + g_{\lambda 1}) \tag{40}$$

We first obtain $\delta_0^{\ 2}$ by evaluating $\sum_\lambda \frac{n_\lambda g_{\lambda 0}}{3}$, a quantity independent of $\delta_0^{\ 2}$. We then evaluate $\sum_\lambda \frac{n_\lambda g_{\lambda 1}}{3}$ until a consistent value of $\delta_0^{\ 2}$ is obtained. Figure (6) shows the result of such calculations. The calculated values fall on a smooth curve which can be fitted, with no discernible deviation, to the formula

$$\delta_0^{\ 2} = 0.99 + 4.22(a - 4.064)^2 \ A^{-2} \tag{41}$$

Formula (41) is characteristic of He^3 in the body-centered cubic lattice, and is valid in the range $3.48 < a < 3.82$. Appendix E is a sample calculation for a point on Fig. 6.

The single-particle representation is therefore

$$\begin{aligned} \gamma_j(\vec{r}_j) &= (\text{const}) \sum_i |\phi_i \ \vec{r}_j|^2 \ e^{-\delta_0^{\ 2} q^2} \\ &\approx (\text{const}) \ e^{-\alpha^2 q^2} \ e^{-\delta_0^{\ 2} q^2} \\ &= (\text{const}) \ e^{-\delta_0^{\ 2} q^2} \ [1 + O(N^{-1/3})] \\ &\approx (\text{const}) \ e^{-[0.99 + 4.22(a - 4.064)^2] q^2} \end{aligned} \tag{42}$$

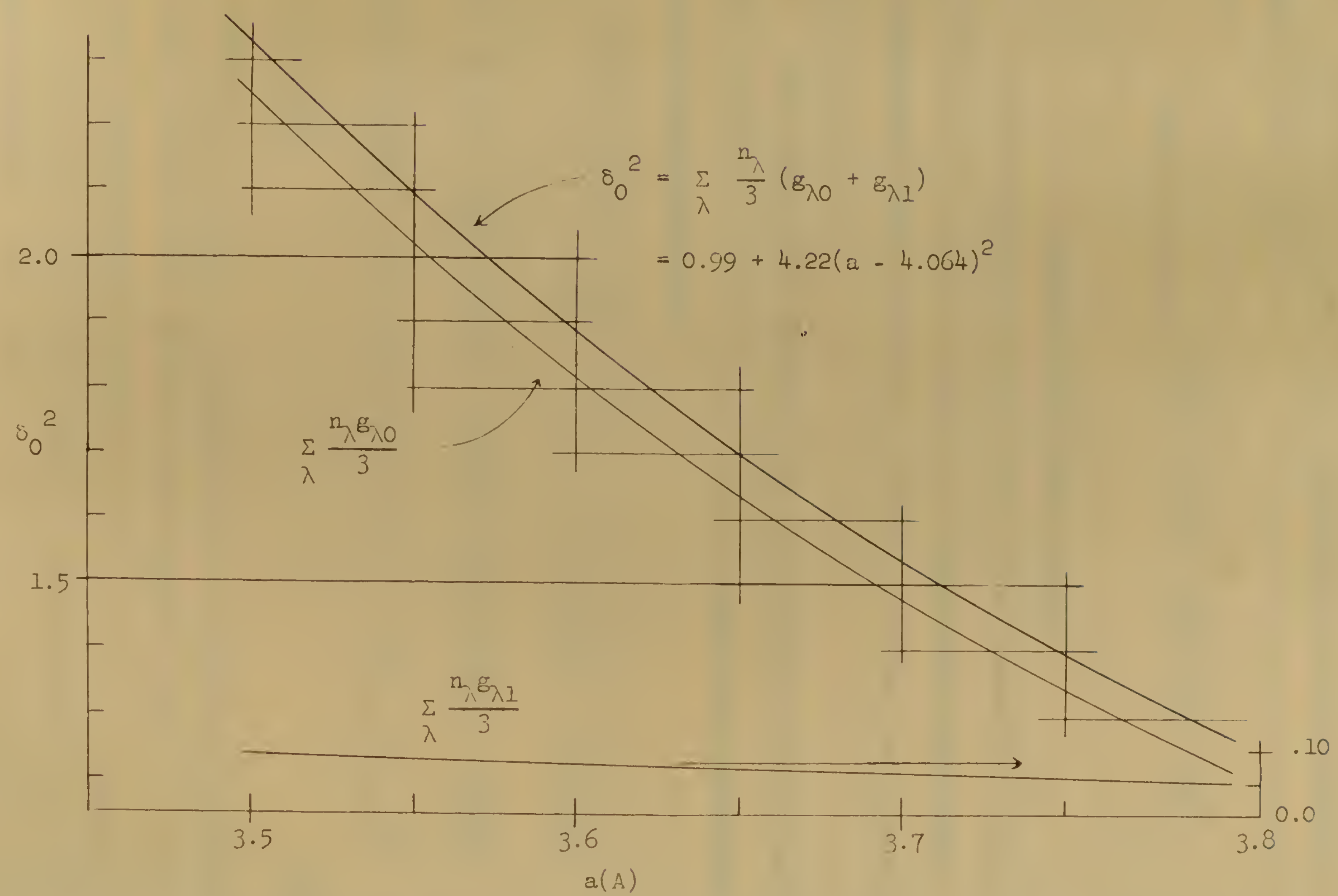


Figure 6. The Probability Density Parameter δ_0^2 Plotted Against Lattice Constant a for Body-Centered Cubic Helium Three.

From (42) we also have the complete single-particle density matrix $\gamma(1) = \sum_j \gamma_j(1)$

$$\gamma(1) = \sum_j (\text{const})\, e^{-[0.99 + 4.22(a - 4.064)^2](\vec{R}_j - \vec{r}_1)^2} .$$

Single-Particle Energy Density

In this section we use the single particle probability density we have obtained in the last section to determine the average energy. The expression contains the lattice constant a through the probability density parameter δ.

Using operators introduced in Eq. (12), together with the density matrix of (13), we can write the N particle energy density matrix in the Pluvinage representation:

$$< E > = \frac{1}{A} \int \sum_i [T_i \left(\frac{\partial}{\partial \vec{r}_i}\right) + V_i(r_i) + \sum_j [T_{ij} \left(\frac{\partial}{\partial r_{ij}}\right) + \frac{1}{2} V_{ij}(r_{ij})$$

$$+ H'_{ij}]] \sum_P P \sum_{P'} P' [\phi_1^*(\vec{X}_1') \phi_2^*(\vec{X}_2') \cdots \phi_N^*(\vec{X}_N') \phi_1(\vec{X}_1) \phi_2(\vec{X}_2) \cdots \phi_N(\vec{X}_N)]$$

$$[\chi_{12}^*(r_{12}') \chi_{13}^*(r_{13}') \cdots \chi_{N-1\,N}^*(r_{N-1\,N}') \chi_{12}(r_{12}) \cdots \chi_{N-1\,N}^*(r_{N-1\,N})]$$

$$d\vec{X}_1\, d\vec{X}_2 \cdots d\vec{X}_N. \tag{43}$$

The normalization integral is represented by A, which has the form of the integral shown in (43), with the energy operator replaced by unity. The prime coordinates permit the wave functions to act as a non-diagonal density matrix under differential operators. We must bear in mind the relationship between the $\vec{X}_i$ and r_{ij} where r_{ij} is a dependent variable

useful in differentiation, as explained in Appendix A. The permutation operator P' permutes the prime coordinates according to Fermi statistics, just as P permutes the unprimed coordinates.

We simplify (43) by noting that the operator $T_{ij} + 1/2\, V_{ij}$ makes no contribution, since $[T_{ij} + 1/2\, V_{ij}]\, \chi_{ij} = 0$ for all i, j. For our symmetry we assume that the term in H' is negligible compared to the term in T. As explained more fully in Appendix F, firstly H' is short range because of the derivative $\partial/\partial r_{ij}$ which vanishes at large r_{ij}, and therefore H' is proportional at most to N and not $N(N-1)/2$. Secondly, in a Bravais lattice, a large part of H' cancels out because H' is linear in relative displacement, and a given atom has a positive displacement with respect to one atom, and an equal and opposite displacement with respect to another atom. A contribution to H' remains which is proportional to the average square of the deviation from the lattice site. In Appendix F we present a plausibility argument that this contribution is considerably less than $\langle T \rangle$.

Taking $V_i(\vec{r}_i)$ to be a constant, we are left with the term $\langle T_i \rangle$:

$$\left\langle \sum_i T_i \right\rangle = \frac{1}{A} \int d\vec{X}_i \sum_i T_i \sum_t \phi_t^*(\vec{X}_i)\, \phi_t(\vec{X}_i)$$

$$\times \Big\{ \sum_P P_S \prod_{\substack{j \neq t \\ m \neq i}} |\phi_j(\vec{X}_m)|^2 \prod_{j < m} \chi_{jm}^2(r_{jm})\, \chi_{im}^2(r_{im})\, d\vec{X}_m \Big\} \quad (44)$$

In (44) we show the symmetric permutation of all the coordinates in the ϕ's in the diagonal representation. Permutations in the diagonal repre-

sentation are the only ones that affect the single-particle operator T_i. (See the last relationship in (5).)

We note that the part in curly brackets is the function $\prod_m \int \gamma(m)\, \chi_{im}(r'_{im})\, \chi_{im}(r_{im}) d\vec{X}_m$. Noting that there are N identical terms in the sum over i (a result of the symmetric permutation generated by $\sum_t \phi_t^2(i)$), we have

$$\left\langle \sum_i T_i \right\rangle = \frac{N}{A} \int d\vec{X}_1\, T_1 \sum_j \phi_j^*(1')\, \phi_j(1)$$

$$\prod_k \int \gamma_k(k)\, \chi_{1k}(r'_{1k})\, \chi_{1k}(r_{1k}) d\vec{X}_k \,. \tag{45}$$

We redefine $f_k(u_{tk})$ in its non-diagonal form:

$$f_k(u_{tk}) = \int \gamma_k(k)\, \chi_{tk}(r'_{tk})\, \chi_{tk}(r_{tk}) d\vec{r}_k \,. \tag{46}$$

So that (45) becomes

$$\left\langle \sum_i T_i \right\rangle_1 = \frac{N}{A} \int d\vec{X}_1\, T_1 \left\{ \left[\sum_j \phi_j^*(1')\, \phi_j(1) \right] \prod_k f_k(u_{1k}) \right\}. \tag{47}$$

When we introduce $\prod_k f_k(u_{1k})$, we evaluate $\left\langle \sum_i T_i \right\rangle_1$, where $\left\langle \sum_i T_i \right\rangle = \sum_j \left\langle \sum_i T_i \right\rangle_j$, since $\prod_k f_k(u_{1k})$ describes the probability density near lattice site 1. This modification results from the same considerations as affected $\gamma(1)$ in Eq. (18). The normalization factor A is

$$A = \int \sum_i |\phi_i(1)|^2 \prod_k f_k(u_{1k}) d\vec{X}_1 . \tag{48}$$

Carrying out the operations in (47), we have

$$\left\langle \sum_i T_i \right\rangle = \left(-\frac{\hbar^2}{2m}\right) \frac{N}{A} \{ \int d\vec{x}_1 \sum_j \phi_j(1) \nabla_1^2 \phi_j(1) \prod_k f_k$$

$$+ \int d\vec{x}_1 \left(\sum_j \phi_j^* \vec{\nabla} \phi_j \right) \cdot \vec{\nabla} (\prod_k f_k)$$

$$+ \int d\vec{x}_1 \sum_j |\phi_j(1)|^2 \sum_t \quad \nu_t(t)\, \chi(r_{1t}) \nabla_1^2 \chi(r_{1t}) d\vec{r}_t$$

$$\prod_{k \neq t,1} f_k(u_{1k}). \tag{49}$$

The brackets in the second term refer to the non-diagonal nature of $\prod_k f_k$. This term of (49) vanishes because $\vec{\nabla} (\prod_k f_k)$ contains a sum over the lattice points k, dotted into the constant vector $\sum_j \phi_j^* \vec{\nabla} \phi_j$. Upon summation, cosine term in the scalar product gives zero.

In the last section we learned we could treat $\sum_j |\phi_j(1)|^2$ as $e^{-\frac{\pi^4 d^2}{8N^{1/3} a^2}}$, hence the first term is expected to be proportional to $N^{-1/6}$, and therefore negligible. In Appendix H we consider this term in detail and verify that it is proportional to $N^{-1/6}$. In the next section we consider exchange, and find that the contribution of the ϕ's to the energy is indeed small, though not proportional to $N^{-1/6}$. The factor $N^{-1/6}$ arises as a direct consequence of neglecting spin and statistics in (49).

The third term will provide the cohesive energy. However, to do the integral over $d\vec{r}_t$, we must apply the constraint $r_{ij} = \sqrt{\vec{s}_{ij} \cdot \vec{s}_{ij}}$

to the X functions. This we do before integration. The operator ∇_1^2 will operate on the result of the integration. Here ∇_1^2 takes derivatives of $X(u_{1j})$ at point 1.

To deal with the integral $\frac{-\hbar^2}{2m} \int \gamma_t(t)\, X_{1t}(r_{1t})\, \nabla_1^2\, X_{1t}(r_{1t}) dr_t$, we identify $\frac{-\hbar^2}{2m} X \nabla^2 X$ with $F(r_{1j})$, and use the result of Appendix C. We show there that any integral of the form $\int \gamma_j(j)\, F(r_{1j}) dr_j$ is given approximately by $F(u_{1j})[1 + 0\; e^{\frac{-\delta^2(u^2-r_0)}{8u}}]$ provided that $F(X)$ is slowly varying near $X = u_{1j}$ compared to the variation in $\gamma(j)$ near $q_j = 0$.

Then, defining the last term of (49) as $\langle T \rangle_{1,8}$,

$$\langle T \rangle_{1,8} = \frac{N}{A}\left(-\frac{\hbar^2}{2m}\right) \int d\vec{X}_1 \left[\sum_j X(u_{1j})\, \nabla_1^2\, X(u_{1j})\right]$$

$$\prod_{k\neq j,1} X^2(u_{1k}) \prod_t \left[1 + 0\left(\frac{e^{-\delta^2(u_{1t} - r_0)^2}}{8\, u_{1t}}\right)\right] \qquad (50)$$

Rewriting (50) and neglecting a derivative $\nabla^2 \sqrt{1 + 0\left(\frac{e^{-\delta^2(u_{1t} - r_0)^2}}{8\, u_{1t}}\right)}$, we get

$$T_{1,8} = \frac{N}{A}\left(-\frac{\hbar^2}{2m}\right) \int d\vec{X}_1 \sqrt{\prod_t f_t(u_{1t})}\; \nabla_1^2 \sqrt{\prod_t f_t(u_{1t})}, \qquad (51)$$

since $f_t(u_{1t}) = X_{1t}^2(u_{1t}) \left[1 + 0\left(\frac{e^{-\delta^2(u_{1t} - r_0)^2}}{8\, u_{1t}}\right)\right]$.

The function $\sqrt{\prod_t f_t(u_{1t})}$ is already known to us from Eq. (25)

$$\rho_1(1) = \sum_i |\phi_i(1)|^2 \prod_t f_t(u_{1t})$$

$$= e^{-\alpha^2 q^2} e^{-\delta^2 q^2} \text{ (const)}$$

or

$$\prod_t f_t(u_{1t}) = \text{(const) } e^{-\delta^2 q^2} . \tag{52}$$

We must consider most carefully the way in which we combine the contributions of the Laplacian operating on each of the f_j, when we employ the representation $e^{-\delta^2 q^2}$. This special attention was also needed in evaluating $\sum_j \Delta_j$ and $\sum_j \Delta_j^2$ in the preceding section.

Each of the $\sqrt{f_j}$ has a single variable u_{1j} or Δ_j for ∇^2 to act upon. Each of the terms in the integral in (50) introduces a "kinetic energy" of relative motion obtained by taking $\partial^2/\partial\Delta_j^2$ (motion normal to the line between 1 and j gives no contribution), and hence represents one degree of freedom. But ∇^2 not only takes derivatives in the direction $\vec{R}_{1j}$, but also two more derivatives of equal value in the two directions normal to $\vec{R}_{1j}$, or would treat each member j as three degrees of freedom. Hence, to use the spherically symmetric matrix $e^{-\delta^2 q_1^2}$ to represent the influence of correlations on the energy of atom 1, in the single particle approximation, we must take 1/3 the result obtained by use of the Laplacian:

$$\langle T_1 \rangle_1 = -\frac{\hbar^2}{2m A}\Big[\int e^{-q_1^2 \delta_0^2} \sum_i \phi_i^*(1)\,\nabla^2 \phi_i(1)\,d\vec{r}_1 \tag{53}$$

$$+ \int \sum_i \phi_i^*(1)\,\phi_i(1)\,\exp(-q_1^2 \delta_0^2/2)\,\frac{\nabla^2}{3}\exp(-q_1^2 \delta_0^2/2)\,d\vec{r}_1\Big]$$

$$A = \int e^{-\delta^2 q_1^2} \sum_i |\phi_i(1)|^2\,d\vec{r}_1. \tag{54}$$

In discussing Eq. (49), we have already seen that the first term of (53) is of order α^2 and hence of order $N^{-1/6}$, and negligible if we neglect overlap and exchange.

Therefore, the single-particle energy, from the second term of (53), is

$$\langle E \rangle = \frac{\hbar^2}{2m}\,\frac{1}{3}\,\frac{3\,\delta_0^2}{2} = \frac{\hbar^2}{4m}\,\delta_0^2\,. \tag{55}$$

Exchange Energy

(a) In this section, using the Pluvinage form of the wave function, we consider the symmetry effects on the magnetic properties of the solid.

Entirely analogous with the treatment of electron exchange, we assume that the Pauli principle applies, so that we are limited to a state description of any pair of particles which is antisymmetric in the interchange of all the coordinates of the pair. We attempt to find the wave function of two-particle states of lowest energy, one symmetric in the space coordinates, corresponding to the triplet spin state and the

other antisymmetric, corresponding to the singlet spin state. The energies of these states are compared, and we obtain the exchange energy.

$$J = E_{+1} - E_{-1} .$$

E_{+1} is the singlet spin state energy, E_{-1} is the triplet energy. Positive J corresponds to parallel spins.

Our calculations will obtain $\langle E \rangle_\eta$ $(\eta = +1, -1)$ and a normalization integral for each case, from which we can construct

$$E_\eta = \frac{\langle E \rangle_\eta}{\langle 1 \rangle_{,\eta}} = \frac{\langle E \rangle + \eta\, \epsilon}{\langle 1 \rangle + \eta\, \Delta} .$$

Then we have:

$$J = \frac{2(\epsilon - \Delta \frac{\langle E \rangle}{\langle 1 \rangle})}{\langle 1 \rangle - \frac{\Delta^2}{\langle 1 \rangle}} . \tag{56}$$

Exchange in the many-body case is somewhat different than in the two-particle case, for which we have just defined J. We define exchange as exchange with respect to a class of neighbors, for example, exchange energy with next nearest neighbors.

We will compare the energy of the solid in two cases--one, when the spins of 1 and the class of neighbors are parallel, and, two, when these spins are antiparallel. If the exchange energy with respect to a given set of neighbors is positive, that exchange integral is termed ferromagnetic.

We proceed by writing down the Hamiltonian. We delete the term $[1/2\, V_{ij} + T_{ij}]$ because it yields zero in the product with χ_{ij}. Accord-

ing to Appendix F, H'_{ij} will appear again as a symmetrically oriented sum, with the linear velocity dependence giving zero to lowest order. We take $V_i(r_i)$ to be a constant. The Hamiltonian (for lowest order exchange energy) is then

$$H = \sum_i T_i \, .$$

We arrange these operators as follows:

$$H = T_1 + \sum_{\lambda}^{M} \sum_{i}^{n_\lambda} T_{i,\lambda} \, . \tag{57}$$

Here, λ includes all of a class of neighbors, like, say, next nearest neighbors of the same spin, which cannot be distinguished within our symmetry of space and spin. We have $\sum_{\lambda}^{M} \sum_{i}^{n_\lambda} 1 = N - 1$.

We now set up the energy-density matrix, as in the preceding section

$$E_\eta = \frac{1}{A_\eta} \int T_1 + \sum_{\lambda}^{M} \sum_{i}^{n_\lambda} T_{i,\lambda} \begin{vmatrix} \phi_{\eta a}(1') & \phi_{\eta a}(2') & \phi_{\eta a}(3') & - - \\ \phi_b(1') & \phi_b(2') & \phi_b(3') & - - \\ \phi_c(1') & \phi_c(2') & \phi_c(3') & - - \\ - & - & - & \diagdown \\ - & - & - & \diagdown \\ - & - & - & \diagdown \end{vmatrix} \begin{vmatrix} \text{same, unprime} \end{vmatrix}$$

$$\prod_{i>j}^{N} \chi_{ij}(r'_{ij}) \, \chi_{ij}(r_{ij}) \, d\vec{X}_1 \ . \ . \ . \ d\vec{X}_N \, . \tag{58}$$

A_η is a normalization integral. Note that a change in η only changes ϕ_a. We are interested in setting up symmetrized states between 1 and

all the other particles. We have no interest in the symmetry of, say, 2 and 3 as a pair, since we do not propose to disturb their symmetry.

We use a form for ϕ_i here which has a natural symmetry for exchange:

$$\phi_i(t) \rightarrow C_{ijk} \cos\left(\frac{\pi x_t}{n_i a}\right) \cos\left(\frac{\pi y_t}{n_j a}\right) \cos\left(\frac{\pi z_t}{n_k a}\right); \tag{59}$$

each wave has a phase to give the greatest symmetry, with no nodes at lattice points. Equation (59) is written for a simple cubic lattice. For other lattices, similar functions can be constructed. For example, in a NaCl type lattice, where the Na represents one spin system and Cl the other, we would have two sets of equation (59), each with $N/2$ members, and each with $a \rightarrow (2/\sqrt{3})a$, the length of the cube edge.

We can rewrite (58), using a Slater determinant which contains only information about the pairs $1 - n$ in antisymmetric states, but which contains no terms giving antisymmetry to the pairs $j - n$, ($j \neq n$, $n \neq 1$). In rewriting (58) we must include the other atoms in a form adequate to construct the contribution to the probability density of the solid from the pairs $j - n$. We can do this by including them as $\sum_j |\phi_j(k)|^2$ ($j \neq 1$). We can use the Slater determinant format, putting zero for all the terms not involving overlap with atom 1. For example, for three particles,

$$P = \begin{vmatrix} \phi_a^*(1) & \phi_a^*(2) & \phi_a^*(3) \\ \phi_b^*(1) & \phi_b^*(2) & 0 \\ \phi_c^*(1) & 0 & \phi_c^*(3) \end{vmatrix} \begin{vmatrix} a(1) & b(1) & c(1) \\ a(2) & b(2) & 0 \\ a(3) & 0 & c(3) \end{vmatrix}$$

$$= A^+ - B^+ - C^+)(A - B - C),$$

where
$$A = \phi_a(1)\ \phi_b(2)\ \phi_c(3)$$
$$B = \phi_a(2)\ \phi_b(1)\ \phi_c(3)$$
$$C = \phi_a(3)\ \phi_b(2)\ \phi_c(1).$$

If we adopt the convention that we drop terms showing overlap of three atoms, the product simplifies to

$$A^+A + B^+B + C^+C - A^+B - A^+C - B^+A - C^+A$$

$$= \left[\sum_P P_s\ |\phi_a(1)|^2\ |\phi_b(2)|\ |\phi_c(3)|^2\right]$$

$$- \{\phi_c^*(3)\ \phi_c(3)\ [\phi_a^+(1)\ \phi_b^+(2)\ \phi_a(2)\ \phi_b(1)$$

$$+ \phi_a^+(2)\ \phi_b^+(1)\ \phi_a(1)\ \phi_b(2)] + (\text{same},\ 2 \to 3,\ 3 \to 2)\}.$$

Hence, we can use the determinant P to consider exchange of 1 and 2, or 1 and 3, but not 2 and 3, nor exchange involving three atoms.

We, therefore, write

$$E_\eta = \frac{1}{A_\eta} \int \left[T_1 + \sum_\lambda^N \sum_i^{n_\lambda} T_{i,\lambda}\right] \begin{vmatrix} \phi_{a_1}(1') & \phi_{a_1}(2') & \phi_{a_1}(3') & \phi_{a_1}(4') & \cdots \\ \phi_b(1') & \phi_b(2') & 0 & 0 & \cdots \\ \phi_c(1') & 0 & \phi_c(3') & 0 & \cdots \\ \phi_d(1') & 0 & 0 & \phi_d(4') & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{vmatrix}$$

$$|\text{same, prime} \to \text{unprime}| \prod_{i>j} \chi_{ij}(r'_{ij})\ \chi_{ij}(r_{ij})\, d\vec{X}_1 \ldots d\vec{X}_N . \qquad (60)$$

If we understand that we include overlap between 1 and only one other atom at a time, for each member of the class λ of indistinguishable members, (60) gives the same result. Using one of the matrix elements out of λ to represent all in λ, we get

$$E_{\eta_1} = \int \frac{T_1}{A_1} + \sum_{\lambda}^{N} n_\lambda \frac{T_\lambda}{A_\lambda} \begin{vmatrix} \phi_{\eta a}(1') & \phi_{\eta a}(2') & \phi_{\eta a}(3') & \phi_{\eta a}(4') & -- \\ \phi_{b,\lambda=1}(1') & \phi_{b,\lambda=1}(2') & 0 & 0 & -- \\ \phi_{c,\lambda=2}(1') & 0 & \phi_{c,\lambda=2}(3') & 0 & -- \\ \phi_{d,\lambda=3}(1') & 0 & 0 & \phi_{d,\lambda=3}(4') & \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{vmatrix}$$

$$\left| \text{same, prime} \rightarrow \text{unprime} \right| \prod_{i > j} \chi_{ij}(r'_{ij}) \, \chi_{ij}(r_{ij}) d\vec{X}_1 \ldots d\vec{X}_N \,. \qquad (61)$$

We calculate the average value of the operators using a different function for each, hence we have a different normalizing constant for each.

We see that T_1 is going to contribute $\langle T_1 \rangle$ to the sum, the value obtained for the direct energy. We can evaluate (61) for any value of λ formally, and obtain a formula. We can apply the formula, once for each λ, adding the results to get the total energy change in changing the spin orientation of 1.

$$E_{\eta,\lambda} - \langle T_1 \rangle = \frac{1}{A_{\eta,\lambda}} \int d\vec{X}_\lambda T_\lambda \begin{vmatrix} \phi_{\eta a}(1') & \phi_{\eta a}(\lambda') \\ \phi_\Lambda(1') & \phi_\Lambda(\lambda') \end{vmatrix} \left| \text{same, prime} \rightarrow \text{unprimed} \right|$$

$$\left[\sum_P P_S \prod_{i \neq a,\Lambda,1,\lambda} \phi_i^2(i) \right] \prod_{i > j,\, i,j \neq \lambda,1} \chi^2(r_{ij}) \prod_k \chi_{1k}(r_{1k}) \, \chi_{1k}(r_{1k}) \, \chi_{\lambda k}(r_{\lambda k}) \chi_{\lambda k}(r_{\lambda k})$$

$$d\vec{X}_k \qquad (62)$$

In (62), we have used only that part of the determinant which describes the symmetrized wave function of the pair (1λ).

We now adopt the convention that the index identifying the spin of a, η, is plus one for the spin of a opposite to Λ, and minus one for the spin of a parallel to Λ. Then, the expression

$$[\phi_a(1)\ \phi_\Lambda(\lambda) + \eta\ \phi_a(\lambda)\ \phi_\Lambda(1)] \tag{63}$$

is antisymmetric in interchange of 1 and λ, and the Pauli principle is obeyed if we use (63) in conjunction with any symmetric function of 1 and λ.

We can rewrite (62), representing all atoms, except 1 and λ, by a single-particle density, as we did in (18) and (45):

$$E_{\eta,\lambda} - T_1 = \frac{n_\lambda}{A_{\eta,\lambda}} \left(-\frac{\hbar^2}{2m}\right) \int [\phi_a^*(1)\ \phi_\Lambda^*(\lambda) + \eta\ \phi_a^*(\lambda)\ \phi_\Lambda^*(1)]\ \chi^2(r_{1\lambda})$$

$$\nabla_\lambda^2 \{[\phi_a(1)\ \phi_\Lambda(\lambda) + \eta\ \phi_a(\lambda)\ \phi_\Lambda(1)] \prod_{k\neq 1,\lambda} \int \gamma_k(k)\ \chi_{1k}^2(r_{1k})$$

$$\times\ \chi_{\lambda k}(r'_{\lambda k})\ \chi_{\lambda k}(r_{\lambda k})\ d\vec{\tau}_k\ \}, \tag{64}$$

with

$$J_\lambda = 2[E_{1,\lambda} - E_{-1,\lambda}]. \tag{65}$$

The factor 2 in (65) arises because of the convention that the exchange energy is the difference in energy for two particles upon exchange, whereas (64) gives the difference for one particle. Formula (64) is the result we would have obtained if we had assumed that if atom 1 and atom 2 give an exchange energy J_{12}, then the total exchange energy for all

neighbors of type 2 is $n_2 J_{12}$, where n_2 is the number of type 2 atoms. However, under this simple assumption, the question arises: how can we include the kinetic energy of atom 1 simultaneously in all the pairs? The derivation (64) answers this question by showing us that the kinetic energy of atom 1 does not affect exchange at all.

The evaluation of (64) is a major task. We can use harmonic oscillator wave functions for the ϕ's. They will include the cut-off effect of the product over k at large distances from the pair (1λ), and will permit the symmetry to be affected by η, if we take one of the states, say λ, to be the first excited state, and the other, say ϕ_a, to be the ground state, in a variable describing the degree of freedom along the line joining the lattice sites of the pair. The function χ^2 can be represented as $\chi^2 = (1 - A e^{-b^2 r_{1\lambda}^2})$, $A = 1.94$, $b = 0.0944/Å^2$. If we handle ϕ and χ^2 in the way described, they yield elementary Gaussian integrals (with complications introduced by the cut off in $\hat{\chi^2}$). Introducing the behavior of the product over k in the region between the lattice sites introduces a crucial problem, in itself worthy of a separate study.

Instead, we calculate an approximate J, valid at low densities, using the single-particle density matrix.

We learned in the last section that we could get $\langle T \rangle$ by putting $\gamma(1'/1) = \sqrt{\gamma(1')\,\gamma(1)}$ (provided only that $\nabla^2\sqrt{1 + O(e^{-\delta^2(u-r_0)}/\delta u)}$ was small). We shall use this idea to reduce the density matrix in (64) to the single particle form. We can interpret the wave function

$[\phi_a(1)\,\phi_\Lambda(\lambda)]\; \chi_{1\lambda}(r_{1\lambda}) \sqrt{\prod_k \int \gamma(k)\, \chi^2(1k)\, \chi^2(\lambda k)\, d\vec{X}_k}$ to be the amplitude for particle 1 to be near lattice site a with particle λ near lattice site Λ. This is because (a) the product over k keeps the particles near these two lattice sites, and (b) $\chi(r_{1\lambda})$ prevents them from being on the same lattice site. We recall that a representation for $\gamma(1)$ was $\sum_j e^{-\delta^2(\vec{R}_j-\vec{r}_1)^2}$. We want to build up a non-diagonal two-particle density matrix from this representation, and still have a result which shows the necessary conditions:

$$\Gamma(1'2'|12) = \Gamma(2'1'|21) = -\Gamma(1'2'|21)$$

$$\Gamma(12|12) = \gamma(1)\,\gamma(2). \tag{66}$$

We recall that we had

$$\gamma(1) = \sum_j \gamma_j(1)$$

$$\gamma_j(1) = (\text{const})\, e^{-\delta^2(\vec{R}_j-\vec{r}_1)^2} .$$

The antisymmetric form of the density matrix which we seek is:

$$\Gamma^{(2)} = \left(\sqrt{\gamma_a(1')\,\gamma_b(2')} + \eta\,\sqrt{\gamma_b(1')\,\gamma_a(2')}\,\right)$$

$$\left(\sqrt{\gamma_a(1)\,\gamma_b(2)} + \eta\,\sqrt{\gamma_a(2)\,\gamma_b(1)}\right)$$

$$= (\text{const})\left[e^{-\frac{\delta^2}{2}\left[(\vec{R}_a-\vec{r}_1{}')^2 + (\vec{R}_b-\vec{r}_2{}')^2\right]} \right. +$$

$$+ \eta\, e^{-\frac{\delta^2}{2}\left[(\vec{R}_a-\vec{r}_2{}')^2 + (\vec{R}_b-\vec{r}_1{}')^2\right]}\Big]\ [\text{same, prime} \rightarrow \text{unprime}]. \quad (67)$$

Formula (67) yields the conditions (66), and gives the correct single-particle effects. Formula (67) would over-estimate the energy if we were to use $-\hbar^2/(2m)\,\nabla_1{}^2$ for the energy operator, in the same way as in Eq. (51). We must introduce the same factor of 1/3 here.

We shall use the form in (67) as a first approximation valid only so long as the spherically symmetric approximation has little effect on overlap of adjacent γ's. The spherically symmetric approximation is poor at small atomic separations, so our results can be expected to have validity only at lower densities.

We can rewrite (67) as $\Gamma^{(2)} = |\psi|^2$,

$$\psi = \left(e^{-\frac{\delta^2}{2}\left[(z_1-b)^2 + (z_2+b)^2\right]} + \eta\, e^{-\frac{\delta^2}{2}\left[(z_1+b)^2 + (z_2-b)^2\right]}\right) e^{-\frac{\delta^2}{2}\left[x_1{}^2 + y_1{}^2 + x_2{}^2 + y_2{}^2\right]}\ . \quad (68)$$

Here $b = a/2$. The z axis joins the two lattice sites 1 and 2, and z_1 and z_2 are measured from the midpoint of the line joining the lattice sites (that is, there are lattice sites at $z = \pm\, b = \pm\, a/2$).

Identifying 2 with λ in (64), and writing the second-order density matrix there in the form (64), we get

$$E_{\eta,2} = \int \psi^* \left(-\frac{\hbar^2}{2m}\right) \frac{\nabla_2{}^2}{3}\ \psi\, dv_1\, dv_2$$

and

$$A_{\eta 2} = \int \psi^* \psi \, dv_1 \, dv_2 = I.$$

We get, performing the operations:

$$\frac{E}{I} = \frac{\hbar^2}{3\cdot 2m} \; \frac{1}{2} \; \frac{\delta^2 - \eta[2\delta^4 b^2 - \delta^2] \; e^{-\delta^2 b^2 (2)}}{(1 + \eta \, e^{-\delta^2 2b^2})}$$

Hence, in Eq. (56), we have

$$\epsilon = \frac{-1 \, \hbar^2}{3\cdot 2 \cdot 2m} [2\delta^4 b^2 - \delta^2] \; e^{-\delta^2 b^2 2}$$

$$\Delta = e^{-\delta^2 2b^2} \quad ,$$

$$\langle E \rangle = \frac{1}{2 \cdot 3} \; \delta^2 \; \frac{\hbar^2}{2m}$$

$$\langle 1 \rangle = 1.$$

We use Eq. (56), but include the factor 2 from (65):

$$J = \frac{2 \times 2 \left(\epsilon - \Delta \frac{\langle E \rangle}{\langle 1 \rangle}\right)}{\langle 1 \rangle - \frac{\Delta^2}{\langle 1 \rangle}} \quad .$$

Neglecting $\Delta^2/\langle 1 \rangle$ compared to $\langle 1 \rangle$, we have

$$J = -\frac{\hbar^2}{m3} [2\delta^4 b^2 - \delta^2 + \delta^2] \, e^{-\delta^2 2b^2}$$

$$J = -\frac{\hbar^2}{3m} \; \delta^2 \; \frac{\delta^2 a^2}{2} \; e^{-\frac{\delta^2 a^2}{2}} \tag{69}$$

Equation (69) cannot be expected to be valid in the high density case, since the overlap of the functions $\gamma(k)$ enters strongly in (69).

A better approximation would consist of using less than spherical symmetry in $\gamma_1(1)$, for example,

$$\gamma_1(1) = e^{-\delta_1^2[(x^2 + y^2 + z^2) + \delta_2^2(x^2y^2 + y^2z^2 + x^2z^2)]}.$$

However, if we anticipate that these corrections to the exchange integral are of the same sign as (69), then (69) gives a lower limit on J.

CHAPTER V

COMPARISON WITH EXPERIMENT

Elastic Effects

In Chapter IV, we have obtained an expression for the cohesive energy of solid He^3 in the body-centered cubic phase:

$$E = \frac{\hbar^2}{4m} \delta_0^2 , \qquad (1)$$

with

$$\delta_0^2 = 1.17 + 4.8 (a - 4.052)^2 \, A^{-2} . \qquad (2)$$

The expression for δ_0^2 is obtained by constructing the ground-state wave function for the given lattice structure from the correlation function $f(r) = F_0(c/r)$, calculating δ_0^2 for various a, and then fitting a curve to a quadratic equation in a.

Formula (1) gives the cohesive energy directly.

Goodkind and Fairbank,[1] and Reich[2] have observed the temperature dependence of the nuclear resonance relaxation times. They use the Bloembergen, Purcell and Pound[3] theory of the diffusion relaxation mech-

[1] J. M. Goodkind and W. M. Fairbank, Helium Three (Edited by J. G. Daunt, Ohio State University Press, Columbus, Ohio, 1960) p. 52.

[2] H. A. Reich, Helium Three (Edited by J. G. Daunt, Ohio State University Press, Columbus, Ohio, 1960) p. 63.

[3] N. Bloembergen, E. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).

anism. The relaxation times follow the Arrhenius law, $T = T_0 e^{-E_A/kT}$, where E_A is the activation energy of diffusion. In Fig. 7, we have plotted the experimental data for the activation energy of diffusion, together with the cohesive energy given by our theory.

To a first approximation, the cohesive energy is the energy to create a vacancy. Once a vacancy exists at low density, little energy is required for the vacancy to move between nearest-neighbor sites, because the next nearest neighbors do not intrude into the space in which diffusion takes place. Hence, the diffusion coefficient (and the relaxation times), should be determined, in the main, by the number of vacancies through the Boltzmann relationship $N = N_0 \exp(- E_{vac}/(kT)$. Here E_{vac} is the energy to create a vacancy in a dilute system of vacancies. Then, if $D \propto N$, $D = D_0 \exp(E_{vac}/(kT)$. The curve indicates general agreement between the diffusion data and our theoretical values of cohesive energy, if we assume that $E_A \cong E \cong E_{vac}$. At high densities the diffusion activation energies lie well above our curve, indicating that our mechanism of diffusion should include a density-dependent activation energy. Our theory cannot treat this problem.

We have attempted to predict the transition to a hexagonal close-packed structure at high densities, using our spherically symmetric single-particle density. This is done by calculating the cohesive energy in the two structures, the structure with lowest energy density being the more stable. Our results are equally valid for hexagonal close-packed and face-centered cubic in the spherically symmetric approximation. This is a better approximation for the 48-fold symmetry of the face-centered cubic

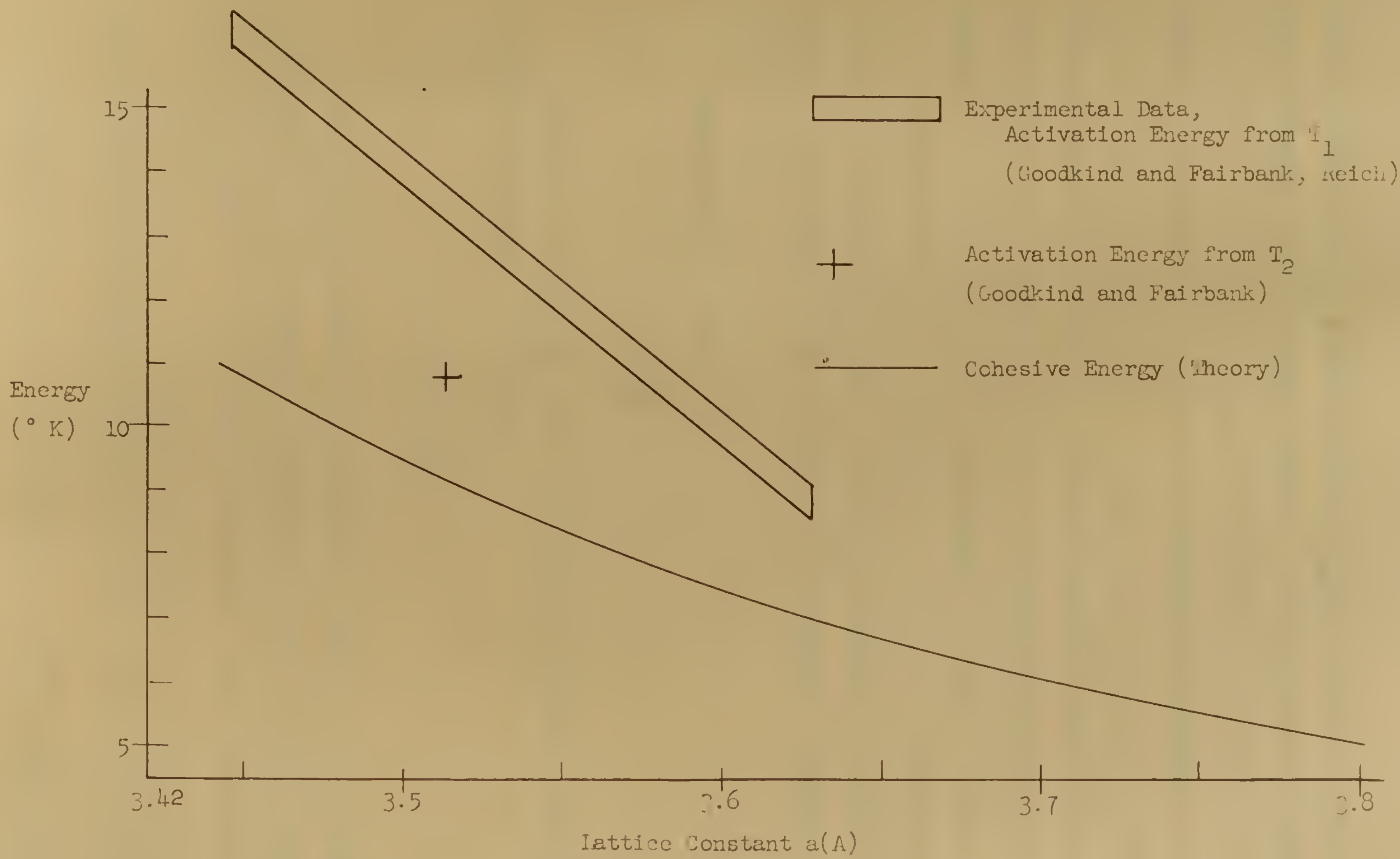


Figure 7. Cohesive Energy and Activation Energy of Nuclear Resonance Relaxation

lattice (with respect to nearest and next nearest neighbor) than for the 6-fold symmetry of the hexagonal lattice. We find the close-packed lattices to be less stable than the body-centered cubic for all densities contrary to experimental findings of a transition to hexagonal close-packed structure at high density. However, the spherically symmetric approximation fails to discriminate between hexagonal close-packed and face-centered cubic lattices, and it is therefore necessary to put the symmetry of the lattice into the single-particle density in order to make a theoretical study of the transition. Because of the expected similarity of close-packed cubic and spherical symmetry, we find the face-centered cubic lattice to be excluded at all densities, compared to body-centered cubic.

The pressure is given by

$$P = -\frac{\partial E}{\partial V} .$$

Hence, $P = -\frac{\partial E}{\partial a}\frac{da}{dV}$. But $V = a^3/1.30$ $Å^3$/atom for a body-centered cubic lattice. Therefore,

$$P = -\frac{1.3}{3a^2}\frac{\partial E}{\partial a} . \qquad (4)$$

In Figure 8 we have plotted pressure, based on (1), (2) and (4). Also plotted are low-temperature experimental points reported by Edwards, Baum, Brewer, Daunt and McWilliams[4] and Sydoriak, Mills and Grilly.[5]

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[4] D. O. Edwards, J. L. Baum, D. F. Brewer, J. G. Daunt, and A. S. McWilliams, Helium Three (Edited by J. G. Daunt, Ohio State University Press, Columbus, Ohio, 1960) p. 128.

[5] S. G. Sydoriak, R. L. Mills, and E. R. Grilly, Phys. Rev. Letter 4, 495 (1960).

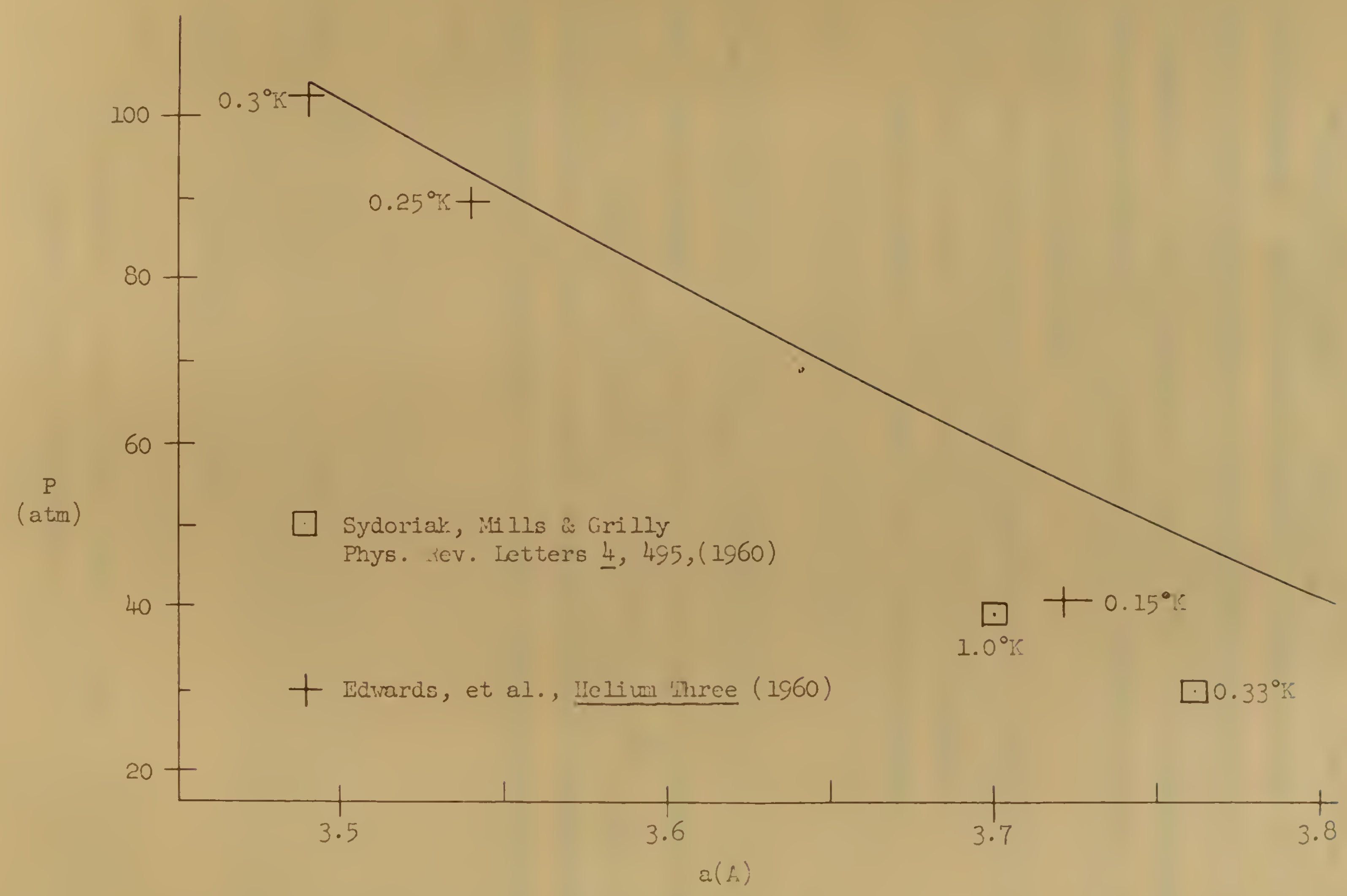

Figure 8. Pressure vs Lattice Constant

Bernardes and Primakoff[6] (B.P.) do not give a theoretical value of the pressure. However, the tabulation of cohesive energy shown in Table II of their paper gives an abrupt change in pressure from positive to negative at a lattice constant of about 3.7 A, with a negative pressure at high densities. Such behavior is not consistent with the small amount of experimental data.

We can calculate the Debye temperature, θ, through the bulk compressibility using an approximation employed by Bernardes.[7]

The bulk modulus is related to the elastic constants

$$\beta = V \frac{dP}{dV} \doteq (c_{11} + 2\, c_{12})/3. \tag{5}$$

We cannot determine c_{11} and c_{12} separately; however, we can assume that we have isotropy $(c_{11} - c_{12} = 2\, c_{44})$, and that the Cauchy relation holds $(c_{12} = c_{44})$. We then have $c_\ell = c_t\sqrt{3} = (c_{11}/\rho)^{1/2}$, where ρ is the density and c_ℓ and c_t are the longitudinal and transverse wave sound velocities. We also have $\beta = 5\, c_{11}/9$. The Debye temperature θ is defined by

$$\theta = h\, c\, (6\, \pi^2\, N/v)^{1/3}, \tag{6}$$

where $3/c^3 = 1/c_\ell^3 + 2/c_t{}^3$. One therefore gets $c = 0.64\, c_\ell$.

We now combine the foregoing assumptions of Bernardes with our value of B to calculate θ. We have

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[6] N. Bernardes and H. Primakoff, Phys. Rev. 119, 968 (1961).

[7] N. Bernardes, Phys. Rev. 120, 807 (1960).

$$\theta = h(0.64)\left[\frac{\beta a}{5\rho}\right]^{1/2}\left[\frac{6\pi^2 N}{V}\right]^{1/3}$$

But $\quad \rho = m(1.3/a^3), \quad N/V = 1.3/a^3, \quad \beta = V\,\frac{1.3}{3a^2}\,\frac{\partial}{\partial a}\,\frac{1.3}{3a^2}\,\frac{\partial}{\partial a}$

$$\beta = +\frac{a^3}{1.3}\left(\frac{1.3}{3a^2}\right)^2\left[\frac{\partial^2 E}{\partial a^2} - \frac{2}{a}\,\frac{\partial E}{\partial a}\right].$$

Combining, we get

$$\theta = 4.86\sqrt{-\frac{2}{a}\frac{\partial E}{\partial a} + \frac{\partial^2 E}{\partial a^2}} \qquad {}^\circ K \text{ (a in A).} \tag{7}$$

Since $\qquad E = 0.99 + 4.22(a - 4.064)^2\ \frac{\hbar^2}{4m}\ A^{-2}$

$$\theta = 4.86\sqrt{4.22\,[a - \frac{1}{a}(a - 4.064)]2 \cdot 4}$$

$$\theta = \frac{57.0}{\sqrt{a}} \quad {}^\circ K \text{ (a in A).} \tag{8}$$

There are no experimental data giving the specific heat. However, near the melting curve, we predict a Debye temperature of 29.2° K, under the assumptions concerning the transverse modes which we described above.

We can also check our results with the findings of Dugdale and MacDonald,[8] that the Lindemann melting formula gives the same value Λ for all inert gases

$$\Lambda = \frac{M\,\theta^2\,V_0^{2/3}}{E_0} = 1.14 \times 10^3 \tag{9}$$

---

[8] J. S. Dugdale and D. K. C. MacDonald, Phil. Mag. 45, 811 (1954) (footnote 4, Chapter II).

M = molar mass, grams/mole

V_0 = molar volume, cm^3/mole

E_0 = molar energy, cals/mole

θ = Debye temperature, ° K.

We can calculate a value of A for very low temperatures. We take a = 3.8 A. Using our value of E and θ for a = 3.8 A, we obtain

$$A = 2.8 \times 10^3.$$

This value is about twice that for other rare-gas solids. However, a factor of 1.4 in θ could cause the discrepancy. Further, He^3 has extreme quantum effects, and (9) may not hold.

Exchange Effects

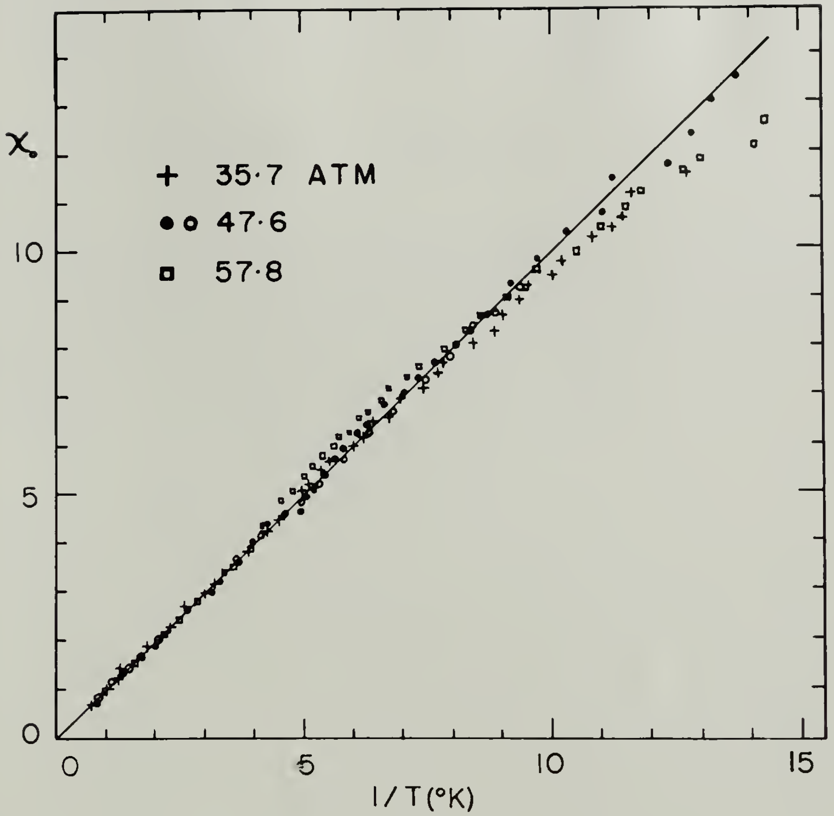
In Chapter IV we have obtained an expression for the exchange energy of solid He^3 in the body-centered cubic configuration, expected to be valid at lower density.

$$J = -\frac{\hbar^2}{3m}\frac{\delta^4 a^2}{2} e^{-\frac{\delta^2 a^2}{2}}. \tag{10}$$

The experimental data of Meyer, Adams and Fairbank[9] can be used to estimate the Curie temperature T_C as a function of lattice constant. Their data are shown in Fig. 9. We estimate T_C by using the definition of T_C contained in the Curie-Weiss law.[10]

[9] E. Dwight Adams, H. Meyer, and W. M. Fairbank, Helium Three (Edited by J. G. Daunt, Ohio State University Press, Columbus, Ohio, 1960) p. 57. The author is indebted to them for making their data available.

[10] J. H. Van Vleck, J. phys. radium 12, 262 (1951).



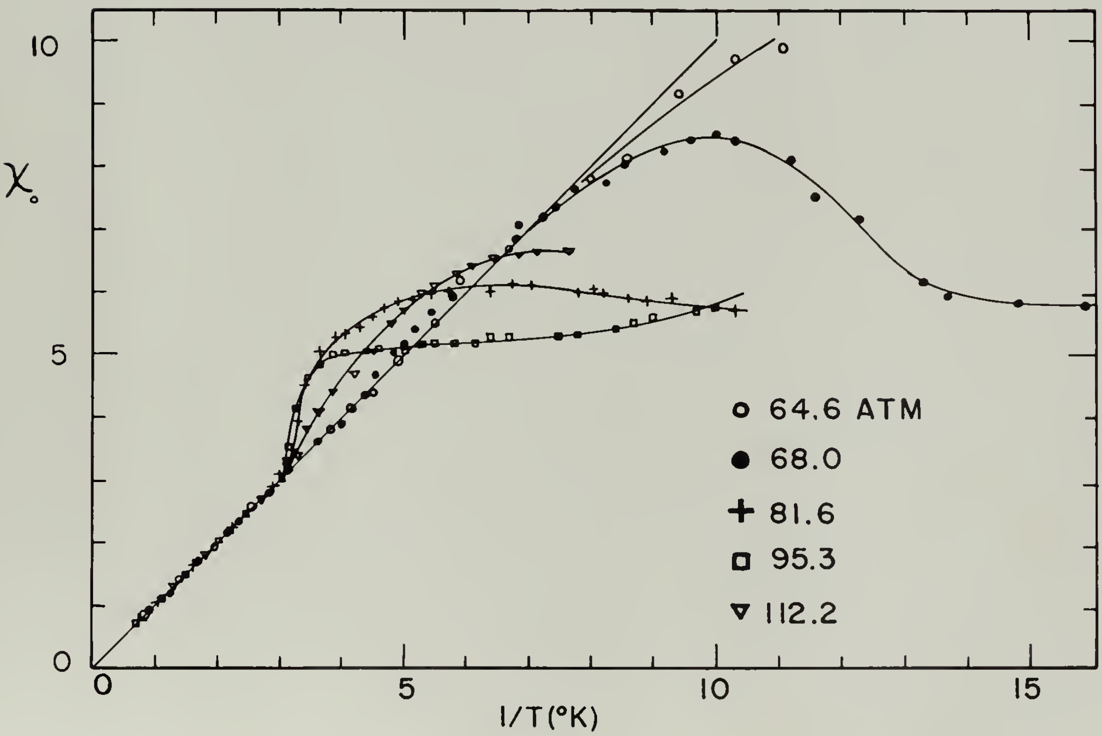


Figure 9

SUSCEPTIBILITY OF SOLID HE^3 FOR VARIOUS PRESSURES VS I/T

$$\chi = \frac{C}{T + T_C} \qquad T > T_C \;, \tag{11}$$

where χ is the magnetic bulk susceptibility, C is the Curie constant for He^3, T is the temperature, and T_C is the Curie temperature. The Curie temperature is given by the exchange energy

$$T_C = \sum_{\lambda} - \frac{J_\lambda n_\lambda}{2} .$$

Here J_λ is the exchange energy (a negative number) with respect to the class of neighbors λ, and n_λ is the number of λ-type neighbors.

We have estimated T_C for various values of a from the experimental data.[8] We obtain the values by replotting the susceptibility as $1/\chi$ against T. The low-pressure curves thus plotted have an unmistakable straight line portion, with a negative intercept on the T axis. This intercept gives the value of T_C, provided that the temperature of the portion of the curve from which the extrapolation was made lies well above T_C. In Fig. 10 we show such a plot for a pressure of 35.7 atm. In Fig. 11 we show the results of several such plots from the data of Fig. 9. The extrapolation process introduces an uncertainty which we have indicated on the figure. On the same figure, we have plotted T_C obtained from our theory. The agreement with experiment is good at large values of the lattice constant, but obviously breaks down for denser solids. Since our theoretical value of J ignores the non-spherical symmetry of the locations of nearest and next nearest neighbors, and does not include the effect of next nearest neighbors on exchange, one would be led to introduce cubic symmetry into $\gamma(1)$ instead of spherical

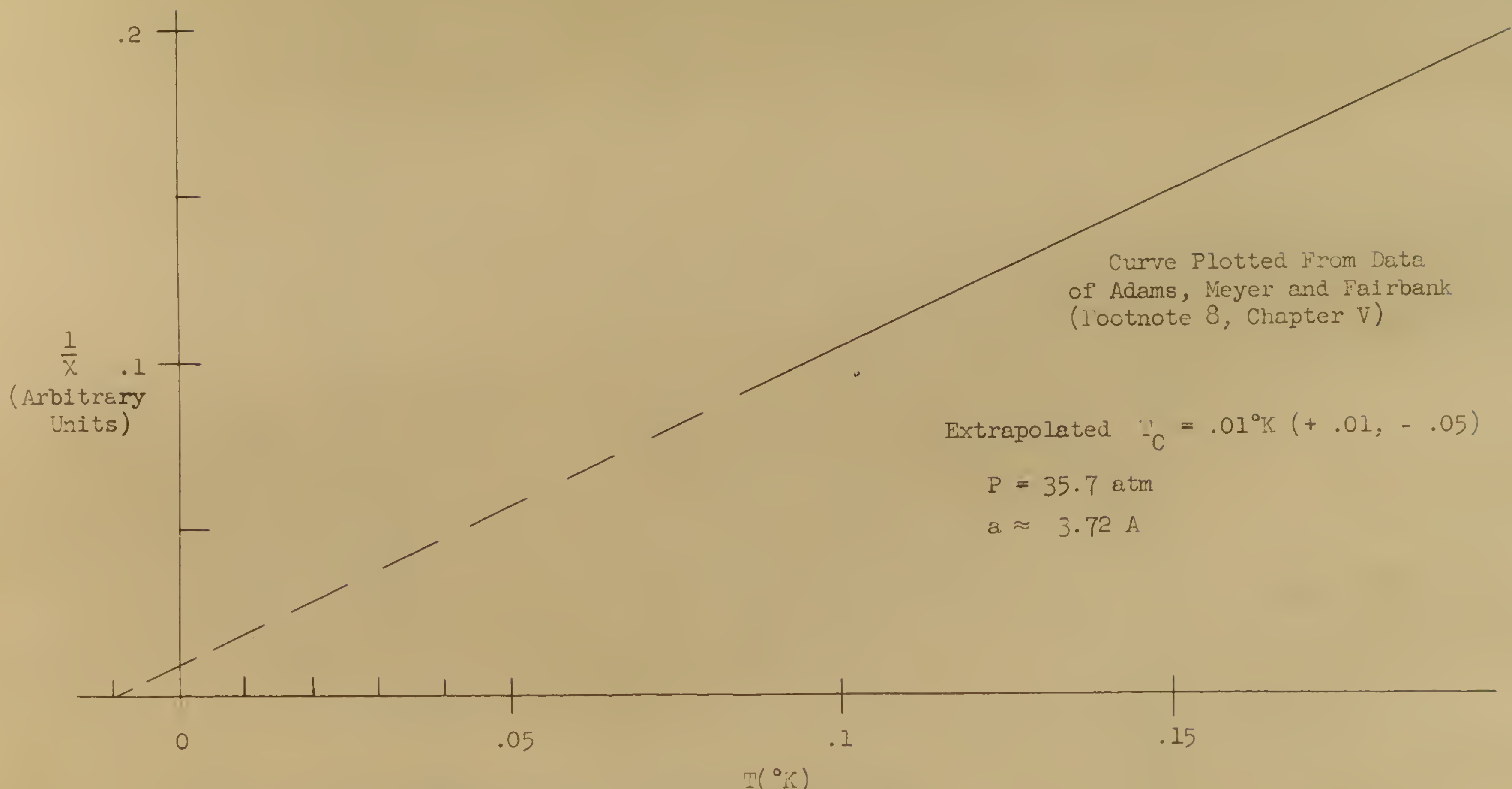


Figure 10 Curie Temperature for Pressure of 35.7 atm.

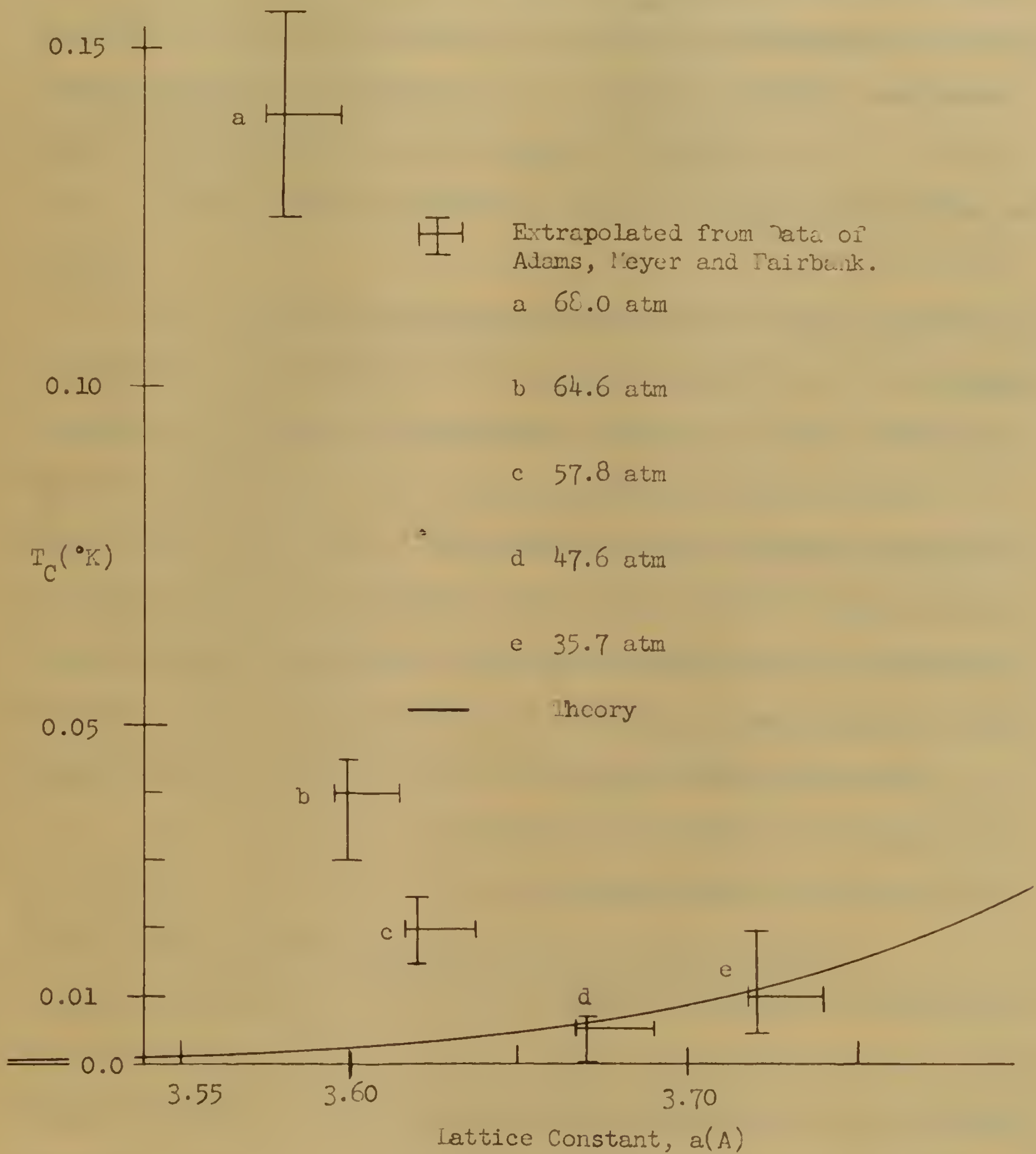


Figure 11. Curie Temperature vs Lattice Constant

symmetry. There would then be a hope of predicting the sharp break in T_C below $a = 3.6$ A as a result of introducing interactions with next nearest neighbors. Calculation of J, using Eq. (IV-64), would also predict the contribution of next nearest neighbors.

We can construct a picture to explain the experimental data, as follows:

(a) At large separations, correlations are relaxed and there is comparatively large overlap of the atomic wave functions. The exchange integral is characteristically negative because the lattice structure and correlations tend to hold the atoms apart in a region where $\partial V(r_{ij})/\partial r_{ij}$ is positive. The symmetric space configuration permits the atoms to be closer together, with a lower potential energy. The kinetic energy is changed but little between the states of differing symmetry. (Note that here we do not rely on the wave function X to carry the interaction, but refer to the interparticle potential.)

(b) As the atoms are brought closer together, correlations become "tighter," the region of overlap between nearest neighbors becomes small, and the exchange integral likewise becomes smaller.

(c) At still lower values of lattice constant, the correlations between nearest neighbors become so "stiff" as to greatly reduce overlap. However, correlations between next nearest neighbors are not as restrictive, and appreciable overlap (and also exchange energy) will exist between them.

All the preceding appears to be substantiated by the behavior of our predicted J with changing lattice constant. We can extend the

[illegible]

At the moment I prefer to explain the experimental data by [illegible]

(a) [illegible]

(b) [illegible]

(c) [illegible]

[illegible]

picture without violating what we have learned from the theory. It is common[10,11] for antiferromagnetic substances, with decreasing temperature, to show a temperature dependent increase of the quantity χT over the constant value of the Curie law, $\chi T = C$. The quantity χT reaches a maximum at the Néel temperature T_N.[12] At lower temperatures, χT falls to zero linearly. This behavior is predicted by the theory[10,11] when interactions with next nearest neighbors are taken into account, in a structure where alternating adjacent crystal planes carry identical spins in each plane, but opposing spins from plane to plane.

Further, it is known[10] that when the sublattices retain their mutual correlations (e.g., nearest neighbors antiparallel, next nearest neighbors parallel) that $\chi(T = 0) = 2/3\ \chi(T = T_N)$. In this expression, T_N is the Néel temperature. If there is no connection between sublattices (e.g., nearest neighbors without correlation, next nearest neighbors antiparallel, or ordering of the second kind), this relationship does not hold.

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[11] C. J. Gorter, Proceedings of the Symposium on Solid and Liquid Helium Three (Ohio State University and Air Force Office of Scientific Research, 1957) p. 199.

[12] The Néel temperature T_N is the temperature below which an antiferromagnetic substance shows magnetic ordering in zero external magnetic field. The Curie temperature T_C is defined as the parameter T_C in the Curie-Weiss law, Eq. (11). In general, $T_N < T_C$, with their ratio (never greater than 3) determined by the relative magnitudes of the exchange interaction between nearest neighbors compared to that between next nearest neighbors. Van Vleck[10] and T. Nagamiya, K. Yosida, and R. Kubo, Advances in Physics 4, 1 (1955) give extensive reviews of antiferromagnetism.

Reference to Fig. 9 shows that the data for 68.0 Atm have a definite maximum at χ = (const) x 8.6, T = 0.1° K. The expected value of $\chi(T = 0)$ if $T_N = 0.1°$ K is then χ = 5.75 (const). The observed value at 0.0625° K is χ = (const) 5.8, and falling slowly. Hence, the data at 68.0 Atm might correspond to an antiferromagnet with a Néel temperature of 0.1° K, with interactions between nearest neighbors and next nearest neighbors of equal importance, conforming to the theoretical prediction[10] that $\chi(T = 0) = 2/3\ \chi(T = T_N)$.

At higher pressures the overlap between nearest neighbors will be reduced still further, and interactions with next nearest neighbors should predominate. Then the relationship $\chi(T = 0) = 2/3\ \chi(T = T_N)$ will no longer hold. The data show no tendency to follow this relationship at high pressures, supporting the conjecture that the exchange interaction with one of the classes of neighbors is very weak compared to that with the other class of neighbors. Our exchange energy becomes small at high density because of small overlap, resulting from the strong exclusion of the correlation function χ^2 at small distances. It can be expected therefore to represent interactions between nearest neighbors. Since it continues to fall as the density increases, we may state that the theory indicates that J (nearest neighbors) is small at high density. Then the observed marked increase in T_C at high density should stem from an exchange interaction with next nearest neighbors. A magnetic transition might occur when the next nearest exchange integral grows large. A specific heat peak at the transition temperature, which might be a comparatively high temperature at elevated pressure, could explain the difficulty in

attaining thermal equilibrium reported by Adams, Meyer, and Fairbank.[9]

Conclusions

Using a two-particle separation of the wave function, we have made an approximate solution for the ground state of solid helium three. We use a description of the solid in a single-particle representation which is determined by the many-body properties of the solid. We adequately predict the density behavior of the cohesive energy of the solid in the body-centered cubic phase. Near the melting curve, we predict an antiferromagnetic Curie temperature of the order of 0.01° K, and at a slightly higher density, a Curie temperature of about 0.005° K, in agreement with experiment.

APPENDICES

APPENDIX A

THE DERIVATIVES OF THE WAVE FUNCTION

WITH INTERPARTICLE PARAMETER[a]

We use the following well-known theorem.

If $f(x^i) = f(x_1, y_1, z_1, x_2, y_2, y_3, \ldots x_N, y_N, z_N, r_{12}, r_{13}, \ldots r_{23}, r_{24}, \ldots r_{N-1,N})$ is a function[b] of n variables, and if the x^i are each differentiable functions of m variables u^i, $u^i = u_1, v_1, w_1, u_2, v_2, w_2$, etc., then

$$\frac{\partial f}{\partial u^j} = \sum_{i=1}^{n} \frac{\partial f}{\partial x^i} \frac{\partial x^i}{\partial u^j} \qquad \text{(A-1)}$$

In our case, we have a spatial wave function $g(u^i) = g(u_1, v_1, w_1, u_2, \ldots v_N, w_N)$, where u, v, and w are the Cartesian coordinates. The number m is therefore $3N$. The Pluvinage wave function is a new function $f(x^i) = f(x_1, y_1, z_1, x_2, \ldots y_N, z_N, r_{12}\ r_{13}, \ldots r_{23}\ r_{24} \ldots r_{N-1,N})$. We make each x^i a function of the u^i

$$x_1 = u_1$$
$$y_1 = v_1$$
$$z_1 = w_1$$
$$\vdots$$

[a]The work of Pluvinage and Walsh and Borowitz displays the Laplacian operator in spherical coordinates. We perform a separate derivation here in order to display the transformation in a form independent of representation.

[b]In our notation, the upper index denotes the entire class of variables. For example, x^i includes x_i, y_i, and z_i, as well as r_{jk}. There is no symbol y^i.

$$r_{12} = \sqrt{(u_1 - u_2)^2 + (v_1 - v_2)^2 + (w_1 - w_2)^2} \qquad \text{(A-2)}$$

etc.

We construct f in this way so that the operators in H can find appropriate variables in f. However, the rules of physics apply to g so we must require that $f = g$ everywhere.

Operations on g using the function f, and not involving derivatives, proceed merely by applying the conditions (A-2). However, if derivatives such as $\partial g/\partial u^{(i)}$ and $\partial^2 g/\partial u^{(i)2}$ are required, we must employ (A-1), then apply (A-2) to the resulting functions, if we wish to use f as an analytical tool.

For example, we obtain $\partial g/\partial v_i$. Since $f = g$ everywhere:

$$\frac{\partial g}{\partial v_i} = \frac{\partial f}{\partial v_i} ;$$

then

$$\frac{\partial g}{\partial v_i} = \frac{\partial f}{\partial v_i} = \sum_{j=1}^{n} \frac{\partial f}{\partial x^j} \frac{\partial x^j}{\partial v_i}$$

$$\frac{\partial f}{\partial v_i} = \frac{\partial f}{\partial y_i} + \sum_{j > k} \frac{\partial f}{\partial r_{jk}} \frac{\partial r_{jk}}{\partial v_i} \qquad \text{(A-3)}$$

This is the rule of differentiation, Eq. III-(6).

To form the second derivative, we employ (A-3) twice:

$$\frac{\partial^2 g}{\partial v_i^{\,2}} = \frac{\partial^2 f}{\partial v_i^{\,2}}$$

$$= \frac{\partial}{\partial v} \quad \frac{\partial f}{\partial y} + \sum_{k} \frac{\partial f}{\partial r_{ik}} \frac{\partial r_{ik}}{\partial v_i} .$$

$$= \frac{\partial^2 f}{\partial y_i^2} + \sum_j \frac{\partial \frac{\partial f}{\partial y_i}}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial v_i} + \sum_k \left(\frac{\partial}{\partial v_i} \frac{\partial f}{\partial r_{ik}} \right) \frac{\partial r_{ik}}{\partial v_i} + \sum_k \frac{\partial f}{\partial r_{ik}} \frac{\partial^2 r_{ik}}{\partial v_i^2}$$

$$= \frac{\partial^2 f}{\partial y_i^2} + \sum_j \frac{\partial^2 f}{\partial r_{ij} \partial y_i} \frac{\partial r_{ij}}{\partial v_i} + \sum_k \frac{\partial^2 f}{\partial v_i \partial r_{ik}} \frac{\partial r_{ik}}{\partial v_i}$$

$$+ \sum_k \sum_j \frac{\partial^2 f}{\partial r_{ij} \partial r_{ik}} \frac{\partial r_{ij}}{\partial v_i} \frac{\partial r_{ik}}{\partial v_i} + \sum_k \frac{\partial f}{\partial r_{ik}} \frac{\partial^2 r_{ik}}{\partial v_i^2}$$

$$\frac{\partial^2 g}{\partial v_i^2} = \frac{\partial^2 f}{\partial y_i^2} + 2 \sum_j \frac{\partial^2 f}{\partial r_{ij} \partial y_i} \frac{\partial r_{ij}}{\partial v_i} + \sum_j \frac{\partial^2 f}{\partial r_{ij}^2} \left(\frac{\partial r_{ij}}{\partial v_i} \right)^2$$

$$+ \sum_{k \neq j} \frac{\partial^2 f}{\partial r_{ij} \, \partial r_{ik}} \frac{\partial r_{ij}}{\partial v_i} \frac{\partial r_{ik}}{\partial v_i} + \sum_j \frac{\partial f}{\partial r_{ij}} \frac{\partial^2 r_{ij}}{\partial v_i^2} \qquad \text{(A-4)}$$

In what follows, we label both the u_i, v_i, w_i and the x_i y_i z_i by x_i, y_i and z_i. We need only to remember that the coefficients $\frac{\partial^n r_{ij}}{\partial v_i^n} \rightarrow \frac{\partial^n r_{ij}}{\partial x_i^n}$ commute with all the differential operators on the right of (A-4). Putting $y_i \rightarrow x_i$, and defining $\sum_x \frac{\partial^2}{\partial x_i^2} = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} = \nabla_i^2$, we obtain the Laplacian. Since $r_{ij}^2 = \sum_x (x_j - x_i)^2$

$$\frac{\partial r_{ij}}{\partial x_i} = \frac{x_i - x_j}{r_{ij}}$$

$$\frac{\partial^2 r_{ij}}{\partial x_i^2} = \frac{1}{r_{ij}} - \frac{(x_i - x_j)^2}{r_{ij}^3} \qquad \text{(A-5)}$$

Putting (A-5) into (A-4),

$$\sum_i \sum_x \frac{\partial^2 g}{\partial x_i^2} = \sum_i \nabla_i^2 g \to \sum_i \left[\sum_x \frac{\partial^2 f}{\partial x_i^2} + \sum_j \sum_x \left[\frac{(x_i - x_j)^2}{r_{ij}^2} \frac{\partial^2 f}{\partial r_{ij}^2} \right.\right.$$

$$\left. + \left(\frac{1}{r_{ij}} - \frac{(x_i - x_j)^2}{r_{ij}^3} \right) \frac{\partial f}{\partial r_{ij}} \right] + \sum_{j,x} \frac{(x_i - x_j)}{r_{ij}} \left[\left(\frac{\partial}{\partial x_i} - \frac{\partial}{\partial x_j} \right) + \left(\frac{\partial}{\partial x_i} + \frac{\partial}{\partial x_j} \right) \right] \frac{\partial f}{\partial r_{ij}}$$

$$\left. + \sum_{j \neq k} \sum_x \frac{(x_i - x_k)(x_i - x_j)}{r_{ik}\, r_{ij}} \frac{\partial}{\partial r_{ij}} \frac{\partial f}{\partial r_{ik}} \right] ; \qquad \text{(A-6)}$$

here, we have separated the term involving $\frac{\partial}{\partial x_i} \frac{\partial}{\partial r_{ij}}$ into its symmetric and antisymmetric parts in i and j. On performing the summation over i and j, we find that only the symmetric part remains.

Performing the summation over x, suppressing f, and noting that $\sum_x (x_i - x_j)^2 = r_{ij}^2$, we obtain

$$\sum_i \sum_x \frac{\partial^2}{\partial x_i^2} = \sum_i \nabla_i^2 \to \sum_i \nabla_i^2 + \sum_i \sum_j \left(\frac{\partial^2}{\partial r_{ij}^2} + \frac{3 - 1}{r_{ij}} \frac{\partial}{\partial r_{ij}} \right)$$

$$+ \sum_i \sum_j \sum_x \frac{(x_i - x_j)}{r_{ij}} \left(\frac{\partial}{\partial x_i} - \frac{\partial}{\partial x_j} \right) \frac{\partial}{\partial r_{ij}} + \sum_{j \neq k} \sum_x \sum_i \frac{(x_i - x_j)(x_i - x_k)}{r_{ij}\, r_{ik}} \frac{\partial^2}{\partial r_{ik} \partial r_{ij}} \qquad \text{(A-7)}$$

We introduce the transformation

$$s_{x,ij} = x_j - x_i \quad \text{(the interparticle displacement)}$$

$$2\, t_{x,ij} = x_j + x_i \quad \text{(the position of the center of mass).}$$

Then $\frac{\partial}{\partial x_i} - \frac{\partial}{\partial x_j} = -2 \frac{\partial}{\partial s_{x,ij}} = -2 \vec{\nabla}_s)_x$,

where

$$\vec{\nabla}_{s,ij} = \frac{\partial}{\partial s_{x,ij}}\,\hat{i} + \frac{\partial}{\partial s_{y,ij}}\,\hat{j} + \frac{\partial}{\partial s_{z,ij}}\,\hat{k}\,,$$

and $\quad (x_i - x_j)(x_i - x_k) = (-\,s_{x,ij})(-\,s_{x,ik}),$

so that $\sum\limits_{x} (x_i - x_j)(x_i - x_k) = \vec{s}_{ij} \cdot \vec{s}_{ik}\,.$

After putting these definitions in (7), we get

$$\sum_i \nabla_i^2 \rightarrow \sum_i \nabla_i^2 + \sum_{ij}{}' \left(\frac{\partial^2}{\partial r_{ij}^2} + \frac{2}{r_{ij}} \frac{\partial}{\partial r_{ij}} \right)$$

$$+ \sum_{ij}{}' \frac{2\,\vec{s}_{ij} \cdot \vec{\nabla}_{s,ij}}{r_{ij}} \frac{\partial}{\partial r_{ij}} + \sum_{i,j,k}{}' \frac{\vec{s}_{ij} \cdot \vec{s}_{ik}}{r_{ij}\,r_{ik}} \frac{\partial}{\partial r_{ik}} \frac{\partial}{\partial r_{ij}} \qquad \text{(A-8)}$$

where $\vec{\nabla}_i$ and $\vec{\nabla}_s$ operate on functions of x, y, z, s and t, and where $\frac{\partial}{\partial r_{ij}}$ acts only on functions of r_{ij}. The constraint $r_{ij}^2 = \vec{s}_{ij} \cdot \vec{s}_{ij}$ is to be used after differentiation. Thereby, after using (A-8) on f, the result is the same as though we had proceeded throughout using the actual function g and the ordinary space derivatives. The primes on the summations indicate that all indices are different on each member of the sum.

APPENDIX B

SOLUTION OF THE CORRELATION AMPLITUDE EQUATION

The correlation amplitude is defined by Eq. II-(16),

$$\left(-\frac{h^2}{m}\ \nabla_r^{\ 2} + V(r)\right)\chi(r) = 0 \qquad \text{(B-1)}$$

$$\nabla_r^{\ 2} = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} \qquad \text{(B-2)}$$

$$V(r) = 4\,\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \qquad \text{(B-3)}$$

where we drop the subscripts, ij from r_{ij}.

We are particularly interested in the solution in the range of r from just inside σ to infinity. An expansion of χ in powers of σ/r will converge in this range, as demonstrated below. Writing (B-1) in detail, we have

$$-\frac{h^2}{m}\left(\frac{\partial^2 \chi}{\partial r^2} + \frac{2}{r}\ \frac{\partial\chi}{\partial r}\right) + 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]\chi = 0 \qquad \text{(B-4)}$$

If $q = \sigma/r$, then

$$\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} = \frac{q^4}{\sigma^2}\ \frac{d^2}{dq^2} \qquad \text{(B-5)}$$

by a straightforward transformation of derivatives. Then (4) has the form

$$q^4\ \frac{d^2\chi}{dq^2} = \frac{m\,\sigma^2\,4\epsilon k}{h^2}\ \left(q^{12} - q^6\right)\chi$$

The variable q will not vanish in the range of interest so we divide by q^4. We also define $B = \frac{m\sigma^2 4ek}{h^2}$, as a factor containing all the physical parameters. For He^3, $B = 16.60$; for He^4, $B = 22.2$.

We must solve

$$\frac{d^2\chi}{dq^2} = B[q^8 - q^2]\chi. \tag{B-7}$$

We attempt a solution:

$$\begin{aligned} \chi = C_0 + C_1 q + C_2 q^2 + C_3 q^3 + \ldots \\ + C_\ell \ln q + C_{-1} q^{-1} + C_{-2} q^{-2} + \ldots \end{aligned} \tag{B-8}$$

Putting (B-8) into (B-7), we obtain conditions on the constants:

$$\begin{aligned}
q^{-2}&: \quad -1\, C_\ell = B\, C_{-10} - B\, C_{-4}\,, \\
q^{-1}&: \quad 0 = B\, C_{-9} - B\, C_{-3},\ C_\ell = 0 \\
\ln q&: \quad 0 = C_\ell \\
q^0&: \quad 2\, C_2 = B\, C_{-8} - B\, C_{-2}\,, \\
q^1&: \quad 3\cdot 2\, C_3 = B\, C_{-7} - B\, C_{-1}\,, \\
q^2&: \quad 4\cdot 3\, C_4 = B\, C_{-6} - B\, C_0\,, \\
q^3&: \quad 5\cdot 4\, C_5 = B\, C_{-5} - B\, C_1\,, \\
q^4&: \quad 6\cdot 5\, C_6 = B\, C_{-4} - B\, C_2\,,
\end{aligned}$$

and so forth.

We expect the solution to approach a constant value independent of q at large $1/q$. Hence, all the coefficients with negative subscripts

must vanish (in other words, we hope to find a function satisfying (7) with $X = C_0 + C_1 q^1 + C_2 q^2 + \ldots$, without negative powers of q).

Setting all the C's with negative indices equal to zero, we obtain:

$$C_0 = C_0 \qquad C_6 = 0$$
$$C_1 = C_1 \qquad C_7 = 0$$
$$C_2 = 0 \qquad C_8 = C_0 B^2/(8\cdot 7 \cdot 4\cdot 3)$$
$$C_3 = 0 \qquad C_9 = C_1 B^2/(9\cdot 8 \cdot 5\cdot 4)$$
$$C_4 = -B\,C_0/4\cdot 3 \qquad C_{10} = C_0 B/(10\cdot 9)$$
$$C_5 = -B\,C_1/5\cdot 4 \qquad C_{11} = C_1 B/(11\cdot 10)$$

$$C_{12} = -\frac{B}{12\cdot 11}\ C_8$$

$$C_{14} = \frac{B}{14\cdot 13}(C_4 - C_{10})$$

$$C_{16} = -\frac{B}{16\cdot 15}(C_{12})$$

$$C_{18} = \frac{B}{18\cdot 17}\ (C_8 - C_{14})$$

$$C_{20} = \frac{B}{20\cdot 19}\ (C_{10} - C_{16})$$

$$C_{22} = \frac{B}{22\cdot 21}\ (C_{12} - C_{18})$$

$$C_{24} = \frac{B}{24\cdot 23}\ (C_{14} - C_{20})$$

$$C_n = \frac{B}{n\cdot(n-1)}(C_{n-10} - C_{n-4}).$$

We shall demonstrate below that the solution carrying the coefficient C_1 is non-physical. Hence we do not display many terms of that solution.

We use the value of B for He^3 ($B = 16.60$), and obtain numerical values of the coefficients as follows:

$$C_4 = -1.391$$
$$C_8 = 4.15 \times 10^{-1}$$
$$C_{10} = 1.855 \times 10^{-1}$$
$$C_{12} = -5.25 \times 10^{-2}$$
$$C_{14} = -1.450 \times 10^{-1}$$
$$C_{16} = 3.65 \times 10^{-3}$$
$$C_{18} = 3.05 \times 10^{-2}$$
$$C_{20} = 8.04 \times 10^{-3}$$
$$C_{22} = -2.74 \times 10^{-3}.$$

We can write the solutions as follows:

$$\chi = C_0 F_0(q) + C_1 q F_1(q)$$
$$F_0 = 1 - B/(4\cdot3)\, q^4 + B^2/(8\cdot7\cdot4\cdot3)\, q^8 + B/(10\cdot9)\, q^{10} + \ldots$$
$$F_1 = 1 - B/(5\cdot4)\, q^4 + B^2/(9\cdot8\cdot5\cdot4)\, q^8 + B/(11\cdot10)\, q^{10} + \ldots$$

At large r, the physical situation corresponds to two helium atoms floating in space, with no tendency for relative motion. We, therefore, expect the total flow in or out of a sphere at a large distance to be vanishingly small.

To a low consistent order in q,

$$\chi(r) \rightarrow C_0 - C_4 q^4 + C_1 q.$$

$$\text{Total Flux} = \lim_{r\to\infty} \int d\Omega \left[C_0 - \frac{C_4 \sigma^4}{r^4} + C_1 \frac{\sigma}{r}\right]\left(-\frac{\hbar i}{m}\right) \vec{\nabla}\left[C_0 - \frac{C_4 \sigma^4}{r^4}\right.$$

$$\left. + C_1\right]\frac{\sigma}{r}\; r^2 = \lim_{r\to\infty} -\frac{4\pi i\hbar}{m}\left[C_0 - \frac{C_4 \sigma^4}{r^4} + C_1 \frac{\sigma}{r}\right]\left[\frac{C_4 \sigma^4 4}{r^5}\right.$$

$$\left. - \frac{C_1 \sigma}{r^2}\right] r^2 = \lim_{r\to\infty} \frac{4\pi \hbar i}{m}\left[- C_0 C_1 \sigma - \frac{C_1 \sigma^2}{r} + \frac{C_0 C_4 \sigma^4 4}{r^3}\right.$$

$$\left. + \ . \ . \ .\right] = -\frac{4\pi i\hbar C_0 C_1 \sigma}{m}\ . \tag{B-9}$$

Now, if $C_0 = 0$, then $\chi(\infty) \to 0$, in violation of the condition that χ not affect the particles at large distances.[a] If $C_0 \neq 0$, and if the flux is to vanish, we have the condition

$$C_1 = 0.$$

---

[a] If we have a bounded system, and the $\phi_i(\bar{r}_i)$ vanish at some finite distance, then the assumption that $\chi_{ij}(r_{ij} \to \infty) = 1$ loses its meaning, since the boundary conditions on the ϕ_i will prevent large values of r_{ij} from occurring. However, for systems with dimensions such that $V >> \sigma^3$, we can assume that we have an unbounded system in setting up the conditions on χ. This condition is not restrictive for the many-body case.

APPENDIX C

NON-LOCAL AVERAGING

In the theory of Chapter IV, we have need of a non-local average of ${X_{ij}}^2$, the square of the correlation function, and of $X_{ij} \nabla_i^2 X_{ij}$, a correlation energy density. In this appendix we derive a general result for the integral

$$\frac{\pi\sqrt{\pi}}{\delta^3} \int e^{-\delta^2 {q_j}^2} F(r_{ij}) d\vec{r}_k = I(u_{ij}). \qquad \text{(C-1)}$$

In Fig. 12 we show the coordinates used in evaluating (C-1). Particle A_j has a displacement $\vec{q}$ from a lattice point j. The particle A_j is described by a probability density proportional to $e^{-\delta^2 {q_j}^2}$. The function $F(r_{ij})$ is some function which is determined by r_{ij}, the distance of A_j from the field point i. It could be, for example, a potential energy or a correlation function. We assume that F is a function with a cut off at r_0:

$$F(r_{ij}) = 0, \quad r_{ij} < r_0 \qquad \text{(C-2)}$$

or

$$F = F(r_{ij})\, \Theta(r_{ij} - r_0).$$

In the second expression in (C-2), we have employed the step function to provide the cut off.

The function $X(r_{ij})$ is given by a series expansion in σ/r, which does not converge for $r < \sigma$. The function $X(r_{ij})$ is known to decrease continuously from $r = \sigma$, and $X(\sigma)$ is very small, so the condition (C-2) is a good description of X for $r < 2.5$ A, and eliminates the problem of non-convergence of $X(\sigma/r)$ in that region.

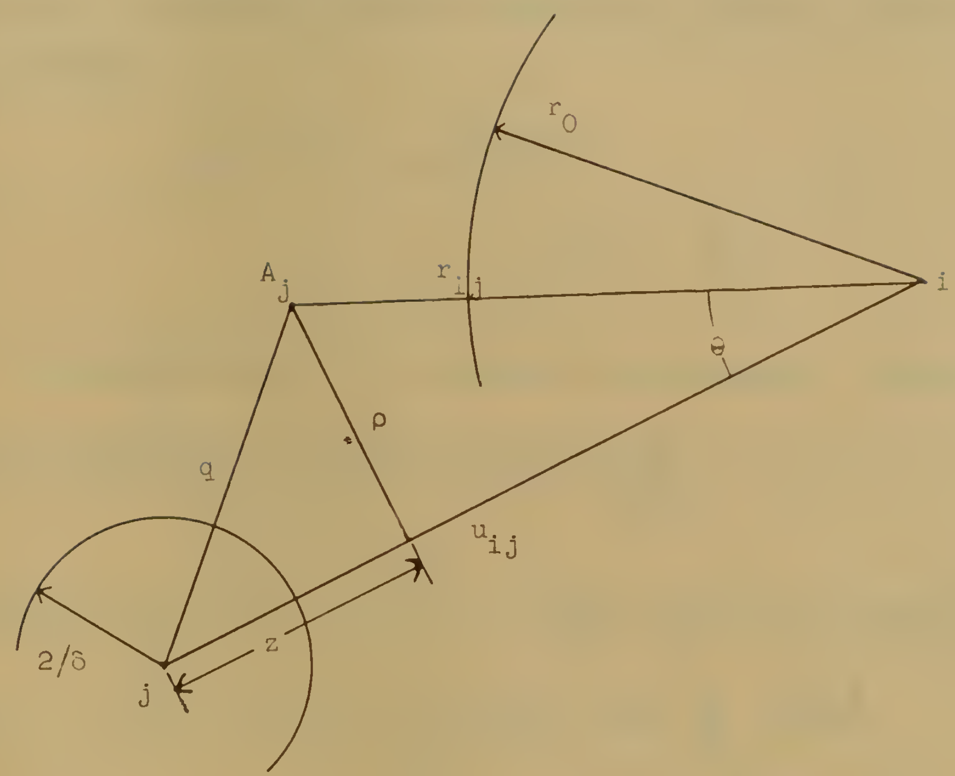

Figure 12. Coordinates for Long Range Averaging Integral

Since we will find that $F(r_{ij})$ is slowly varying near $r_{ij} = u_{ij}$ we will expand $F(r_{ij})$ about the point j. The resulting expression will be a function of u_{ij}, the distance from the lattice point j to the field point i. Using the auxiliary variables z and ρ, to the order shown, we have

$$F(r) = F(u - z - \frac{z^2 + \rho^2}{2u})$$

$$= F(u) - (z + \frac{\rho^2 + z^2}{2u})F' + \frac{z^2}{2} F'' + \ldots .$$

We integrate the first two terms of the expansion. First, we have:

$$I_1 = F(u) \int e^{-\delta^2 q^2} \theta(r - r_0) r^2 \, dr \, d(\cos\theta) \, 2\pi \frac{\delta^3}{\pi\sqrt{\pi}}$$

$$= 2\pi F(u) \int e^{-\delta^2(u^2 + r^2 - 2ru\cos\theta)} \theta(r - r_0) r^2 \, dr \, d\cos\theta \, \frac{\delta^3}{\pi\sqrt{\pi}} .$$

We have $\displaystyle\int_c^\infty e^{-a^2x^2 + bx} x \, dx = \frac{1}{2a^2}\left[e^{-a^2c^2} e^{cb} + \frac{b}{a} e^{b^2/4a^2}\right.$

$$\left. \times \frac{\sqrt{\pi}}{2}\left[1 - \Phi\left(ac - \frac{b}{2a}\right)\right]\right].$$

So, we get

$$F(u) \frac{1}{2u\delta\sqrt{\pi}} \left[e^{-\delta^2(r_0 - u)} - e^{-\delta^2(r_0 + u)}\right]$$

$$+ F(u) \frac{1}{2} [1 - \phi[\delta(r_0 - u)] + 1 - \phi[\delta(r_0 + u)]].$$

Now, we will find that $\delta^2 > 1$, $r_0 = 2.5$, so that $r_0 + u$ can be considered to be very large, and we get

$$F(u)\left[\frac{1}{2}\,[1 + \phi\,[\delta(u - r_0)]] + \frac{e^{-\delta^2(r_0 - u)^2}}{2\sqrt{\pi}\,\delta u}\right].$$

We next consider the term containing $F'(u)$. Since we neglected terms with $[\delta(r_0 + u)]$ in evaluating the leading term, we are justified in doing so at the outset here, and evaluate

$$I_2 = -F'(u)\int e^{-\delta^2 q^2}\left(z + \frac{\rho^2 + z^2}{2u}\right)\theta(u - r_0 - q)dv\,\frac{\delta^3}{\pi\sqrt{\pi}}$$

$$= -F'(u)\,\frac{2\,\delta^3}{u\sqrt{\pi}}\int_{u-r_0}^{\infty} e^{-\delta^2 q^2}\,q^4\,dq$$

$$= -F'(u)\,\frac{\delta^3\,2}{u\sqrt{\pi}}\left[\frac{3\sqrt{\pi}}{8\,\delta^5}\,[1 + \phi(\delta[u - r_0])] + \frac{u - r_0}{2\delta}\,e^{-\delta^2(u - r_0)^2}\right.$$

$$\left.\times\left(\frac{3}{2\,\delta^2} + (u - r_0)^2\right)\right].$$

Then

$$I_2 = -F'(u)\left[\frac{3}{4\,\delta^2}\,[1 + \phi(\delta[u - r_0])] + \frac{(u - r_0)}{2\sqrt{\pi}}\,[3 + 2\delta(u - r_0)^2]\right.$$

$$\left.\times\; e^{-\delta^2(u - r_0)^2}\right].$$

We have the result

$$\frac{\int e^{-\delta^2 q^2}\,F(r)\,\theta(r - r_0)dv}{\int e^{-\delta^2 q^2}\,dv} = \left[F(u) - \frac{3\,F'(u)}{2\,\delta^2\,u}\right][1 + \phi[\delta(u - r_0)]]\,\frac{1}{2}$$

$$+\left[\frac{F(u)}{} - F'(u)(u - r_0)(3 + 2\delta(u - r_0)^2\right]\,\frac{e^{-\delta^2(u - r_0)^2}}{2\sqrt{\pi}}$$

$$+\;O\,(F''(u)). \qquad \text{(C-3)}$$

Equation (C-3) can be used to check the validity of approximations used in evaluating the integral. Ordinarily we will use the leading term.

APPENDIX D

CALCULATION OF THE TERMS OF THE EXPONENTIAL SUM

We calculate $\varepsilon_\lambda = \varepsilon_{\lambda 0} + \varepsilon_{\lambda 1} + \varepsilon_{\lambda 2}$, where

$$\varepsilon_\lambda = \left[\frac{1}{u} + \frac{1}{2}\frac{d}{du}\right] \frac{f'}{f}\Big|_{u=r_\lambda} \tag{D-1}$$

from Eq. IV-(17). For f, we have

$$f = \frac{1}{2}\chi^2(u)[1 + \Phi(\delta[u - r_0])] + O\left[\left(\frac{\chi\chi'}{\delta^2 u}\right), \left(\frac{\chi^2}{\delta u} e^{-\delta^2(u - r_0)^2}\right)\right]; \tag{D-2}$$

For values of u which we consider, the second term is always much smaller than the first, so that the denominator of f'/f can be taken to be the leading term of (D-2).

We define $f_\chi = \chi^2(u)$, $f_\delta = \frac{1}{2}[1 + \Phi(\delta[u - r_0])]$. Excluding terms of order $\frac{\chi\chi'}{\delta^2 u}$, we have

$$\frac{f'}{f} \approx \frac{(f_\chi f_\delta)'}{f_\chi f_\delta} = \frac{f'_\chi}{f_\chi} + \frac{f'_\delta}{f_\delta}.$$

The first of these in (D-1) gives $\varepsilon_{\lambda 0}$; the second contributes to $\varepsilon_{\lambda 1}$. The correction term, $\varepsilon_{\lambda 2}$ is of higher order in $1/\delta$ and χ', and accordingly neglected. First, we use the series expansion representation for χ

$$X = 1 - \frac{B\,\sigma^4}{12\,r^4} + \frac{B^2\,\sigma^8}{56\cdot 12\,r^8} + \frac{B}{90}\,\frac{\sigma^{10}}{r^{10}} - \frac{B^3}{121\cdot 56\cdot 12}\,\frac{\sigma^{12}}{r^{12}} + \dots \tag{D-4}$$

Noting that $f'_X/f_X = X^{2\prime}/X^2 = 2\,X'/X$, we get

$$\frac{f'_X}{f_X} = \frac{2\,B\,\sigma^4}{r^5}\left[\frac{1}{3} + \frac{B\,\sigma^4}{r^4}\,\frac{1}{9\cdot 7} - \frac{\sigma^6}{9\,r^6} + \frac{2}{33\cdot 63}\,\frac{B^2\,\sigma^8}{r^8} + \dots\right],$$

by differentiating (D-4), and then dividing by X. We next form $[1/u + 1/2\ d/du]\ f'/f$, getting

$$\varepsilon_{\lambda 0,1} = -\frac{B\,\sigma^4}{r^6}\left[1 + \frac{B\,\sigma^4}{9\,r^4} - \frac{\sigma^6}{r^6} + \frac{B^2\,\sigma^8}{r^8}\,\frac{2}{105} + \dots\right]. \tag{D-5}$$

As a check on (D-5), we can also use the Yukawa representation for X, $X = 1 - (r_0/r)\exp(-\gamma(r - r_0))$.

$$\frac{2\,X'}{X} = \frac{2e^{-\gamma(u-r_0)}\left[\dfrac{1+\gamma u}{u}\right]\dfrac{r_0}{u}}{1 - \dfrac{r_0}{u}\,e^{-\gamma(u-r_0)}} = \frac{2(1+\gamma u)}{u}\,\frac{[1 - X]}{X}.$$

Now, $\dfrac{d}{du}\,\dfrac{1 - X}{X} = \dfrac{X(-X') - (1 - X)X'}{X^2} = -\dfrac{X'}{X^2}$,

and

$$X' = \frac{1 + \gamma u}{u}\,(1 - X).$$

Therefore,

$$\varepsilon_{\lambda 0,2} = -\frac{1 - X}{Xu^2}\left[\frac{(1 + \gamma u)^2}{X} - (1 + 2\,\gamma u)\right]. \tag{D-6}$$

We obtain the correction term $\varepsilon_{\lambda 1}$ by writing out f' to second order: From the result of Appendix C, if we call $F(r_{ij}) = X^2(r_{ij})$, then

$$f_1 = (\text{const}) \int e^{-\delta^2 q^2} \chi^2(r_{ij})d\vec{r}_j$$

$$= \left(\chi^2(u) - \frac{3\,\chi'\chi}{\delta^2 u} \right) [1 + \phi[\delta(u - r_0)]]\frac{1}{2}$$

$$+ \left(\frac{\chi^2(u)}{\delta u} - \chi'\chi(2)\;(u - r_0)(3 + 2\delta(u - r_0)^2) \right) \frac{e^{-\delta^2(u - r_0)^2}}{2\sqrt{\pi}}$$

Excluding terms from f' like $\chi'\chi\, e^{-\delta^2(u - r_0)^2}(u - r_0)$ and $\chi''\chi$, we have for the terms in χ^2 and the leading terms in $\chi'\chi$

$$f' = 2\,\chi\chi'[1 + \phi(\delta[u - r_0])]\,\frac{1}{2}$$

$$+ [\chi^2]\,\frac{\delta}{\sqrt{\pi}}\quad e^{-\delta^2(u - r_0)^2} + \left[-\frac{\chi^2}{\delta u^2}\right] \frac{1}{2\sqrt{\pi}}\; e^{-\delta^2(u - r_0)^2}$$

$$+ \left[\frac{\chi^2}{\delta u}\right] \frac{(\delta^2(u - r_0)2)}{2\sqrt{\pi}}\; e^{-\delta^2(u - r_0)^2} + \text{smaller terms.}$$

Hence the leading terms in f' are

$$f' = \chi'\chi[1 + \phi[\delta(u - r_0)]]$$

$$+ \frac{\chi^2\, e^{-\delta^2(u - r_0)^2}}{\sqrt{\pi}} \left(\delta - \delta + \frac{\delta r_0}{u} - \frac{1}{\delta u^2 2} \right).$$

So that

$$\epsilon_{\lambda 1} = \left[\frac{1}{u} + \frac{1}{2}\frac{d}{du}\right] \frac{e^{-\delta^2(u - r_0)^2}}{\sqrt{\pi}} \frac{\left(\frac{\delta r_0}{u} - \frac{1}{2\,\delta u^2}\right)}{1 + \phi[\delta(u - r_0)]}$$

If we exclude terms with $\exp(-2\,\delta^2(u - r_0)^2)$, we get

$$\varepsilon_{\lambda 1} = \frac{e^{-\delta^2(u - r_0)^2}}{\sqrt{\pi}\,(1 + \phi[\delta(u - r_0)])}\left[\frac{\delta r_0}{u^2} - \frac{1}{2\,\delta u^3} + \frac{1}{2}\left[\left(\frac{\delta r_0}{u} - \frac{1}{2\,\delta u^2}\right)\left(-2\delta^2(u-r_0)\right)\right]\right.$$

$$\left. - \frac{\delta r_0}{u^2} + \frac{3}{2\,\delta u^3}\right] \cong - \frac{e^{-\delta^2(u - r_0)^2}}{\sqrt{\pi}(1 + \phi[\delta(u - r_0)])}\left(\frac{\delta^3\, r_0(u - r_0)}{2u}\right) \quad \text{(D-7)}$$

In arriving at this correction term, we find that all the contributions in δ to the leading term in f' have cancelled with terms from the second term in f'. This correction term in δ arises from the cut off in χ^2. There is also a correction term arising from the slope of χ^2 in the region where the Gaussian $\exp(-\delta^2 q^2)$ is large, but this term is of order $\left(\frac{\chi\chi'}{u}\right)'/\delta^2$ compared to χ^2, and we have discarded a term of this order in arriving at (D-7). We will use the correction term (D-7), but consider our uncertainty in results to be of the order of the change in results brought about by (D-7).

APPENDIX E

SAMPLE CALCULATION OF δ^2

We illustrate the method used in constructing Fig. 6 by evaluating the points at $a = 3.6$ Å.

We first evaluate the sum $\sum_\lambda \frac{n_\lambda g_{\lambda 0}}{3}$ using the series expansion form of IV-(37) plotten in Fig. 5.

λ	n_λ	R_λ/a	R_λ	$g_{\lambda 0}$ (Fig. 5)	$\frac{n_\lambda g_{\lambda 0}}{3}$
1	8	1.0	3.60	0.490	1.31
2	6	1.154	4.16	0.18	0.36
3	12	1.637	5.89	0.017	0.07
4	24	1.918	6.80	0.0076	0.06
5	8	2.0	7.20	0.0052	0.01
6	6	2.315	8.31	0.0022	
7	24	2.480	8.93		
					1.81

We now calculate the correction term $\sum_\lambda \frac{n_\lambda}{3} g_{\lambda 1}$. Assume that $\delta^2 = 1.88$, $r_0 = 2.5$

$$g_{\lambda 1} = - \frac{e^{-\delta^2(R_\lambda - r_0)^2}}{\sqrt{\pi}(1 + 0[\delta[R_\lambda - r_0]]} \quad \frac{\delta^3 r_0 (R_\lambda - r_0)}{2 R_\lambda}$$

$$= - \frac{.102 \cdot 2.58 \cdot 2.5 \cdot 1.1}{1.73 \cdot 2.0 \cdot 2 \cdot 3.6} = .029; \; .029 \times \frac{8}{3} = .077$$

$$\delta^2 = 1.81 + .077 = 1.89 \text{ check.}$$

APPENDIX F

THE CONTRIBUTION TO THE ENERGY OF THE PLUVINAGE PERTURBATION

We consider the term in IV(43) which gives the energy of the Pluvinage Perturbation

$$H_{ij} = -\frac{h^2}{2m} 2\, \vec{s}_{ij} \cdot \vec{\nabla}_{s,ij} \frac{1}{r_{ij}} \frac{\partial}{\partial r_{ij}}$$

$$- \sum_k{}' \frac{h^2}{2m} \frac{\vec{s}_{ij} \cdot \vec{s}_{ik}}{r_{ij}\, r_{ik}} \frac{\partial^2}{\partial r_{ij}\, \partial r_{ik}} \qquad \text{(F-1)}$$

Then, neglecting exchange effects $\left\langle \sum_k H'_{pk} \right\rangle =$

$$\frac{1}{A} \sum_{p,k} \int d\vec{X}_p\, d\vec{X}_k \quad H'_{pk} \left[\frac{1}{2} \sum_{i,j}{}' \phi_j^*(p')\, \phi_j(p)\, \phi_i^*(k')\, \phi_i(k) \right]$$

$$\chi_{pk}(r'_{pk})\, \chi_{pk}(r_{pk}) \sum_P P_S \left[\prod_{t \neq p,k} |\phi_t(t)|^2 \right] \left[\prod_{\substack{t,r \neq p,k \\ r < t}} \chi_{rt}^2\, \chi_{pt}^2\, \chi_{kt}^2\, d\vec{X}_t \right] \qquad \text{(F-2)}$$

with

$$A = \int \sum_P P_S \left[\prod_t |\phi_t(t)|^2 \right] \prod_{t > r} \chi_{rt}^2\, d\vec{X}_t$$

$$= \int d\vec{X}_p \sum_j |\phi_j(p)|^2 \prod_k \int \gamma(k)\, \chi_{pk}^2\, d(\vec{X}_k) \qquad \text{(F-3)}$$

We use the single particle density matrix to represent all the particles except p and k:

$$\left\langle \sum_{p,k} H_{pk} \right\rangle = \frac{1}{A} \sum_{p,k} \int d\vec{x}_p \, d\vec{x}_k \, H'_{pk} \left[\frac{1}{2} \sum_{i,j}{}' \phi_i^*(p') \, \phi_i(p) \, \phi_j^*(k') \, \phi_j(k) \right]$$

$$X_{pk}(r'_{pk}) \, X_{pk}(r_{pk}) \prod_{t \neq k,p} \int Y_t(t) \, X^2_{pt} \, X^2_{kt} \, d\vec{x}_t \; . \qquad \text{(F-4)}$$

In (F-4), the product over t is non-diagonal so that H'_{pk} may operate.

We now present an argument that the numerator of (F-4) vanishes to lowest order in the energy, in a Bravais lattice. Let us consider atoms 1, 2, and 3 arranged on lattice sites 1, 2, and 3 in one of the lines that define the Bravais lattice. We have for their contribution to H', from the first term in H'

$$\left[H'(1) \right]_{123} = \text{Const} \int dx_1 dx_2 (x_1 - x_2) \left(\frac{\partial}{\partial x_1} - \frac{\partial}{\partial x_2} \right) |f(r_{12})| \; g(1,2)$$

$$+ \text{Const} \int dx_2 dx_3 (x_2 - x_3) \left(\frac{\partial}{\partial x_2} - \frac{\partial}{\partial x_3} \right) |f(r_{23})| \; f(2,3) \qquad \text{(F-5)}$$

Here $|f(r_{12})| = X(r_{12}) \, X'(r_{12})/r_{12}$, and

$$g(i,j) = g(j,i) = \sum_{k,m}{}' \phi_k^2(i) \, \phi_m^2(j) \prod_{p \neq i,j} \int Y(p) \, X^2_{ip}(r_{ip})$$

$$X^2_{jp}(r_{jp}) d\vec{x}_p \; .$$

In (F-5), we have put the x axis along the line joining the lattice sites, and assume cylindrical symmetry, so that $y_1 - y_2$ and $z_1 - z_2$ average to zero.

We exclude the derivatives $\frac{\partial}{\partial x_1}$ and $\frac{\partial}{\partial x_3}$ from consideration, because they will appear in other pairs of equations. In (F-5), x_2 describes the position of the same particle simultaneously in both integrals. We therefore take $x_1 > x_2 > x_3$.

We estimate the value of (F-5) by writing the integrals in the numerator in the same form as the normalization integral, by assigning estimated values to the operators and expressions there.

$$\left[E'_{(1)}\right]_{123} = -\frac{\hbar^2}{2m}\left(\int dx_2\ [\int dx_1\ [a + x_1' - x_2']\ \left(-\frac{\partial}{\partial x_2}\right)|f(r_{12})|\ g(1,2)\right.$$

$$\left. + \int dx_3[-a + x_3' - x_2']\ \left(-\frac{\partial}{\partial x_2}\right)\ |f(r_{32})|\ g(2,3)]\right)$$

$$\times\ \left(\int dx_2\ dx_1\ x_{12}^2\ g(1,2)\right)^{-1} . \qquad (F\text{-}6)$$

In (F-6), we have taken advantage of the fact that on the average x_1, x_2 and x_3 are at their lattice sites.

The parts of the integral containing a vanish as the difference of two equal quantities. The integrals containing x_1' and x_3' vanish because x_1' and x_3' are odd functions.

We are therefore left with

$$\left[E'_{(1)}\right]_{123} = -\frac{\hbar^2}{2m}\left(\int dx_2\ [\ \int dx_1\ [x_2'\ \frac{\partial}{\partial x_2}\ \ |f(r_{12})|\ g(1,2)\right.$$

$$\left. + \int dx_3\ x_2'\ \frac{\partial}{\partial x_2}\ \ |f(r_{32})|\ \ g(2,3)]\right)\left(\int dx_1 dx_2\ x_{12}^2\ g(1,2)\right)^{-1} \qquad (F\text{-}7)$$

We now assign estimated values to the quantities in the integral of the numerator:

$$\frac{\partial}{\partial x_2} g(1,2) \approx -\frac{x_2' \delta^2}{2}$$

$$f(r_{12}) \approx .1 \ \chi_{12}^2 \ A^{-2}$$

$$\frac{(x_2)^2 \delta^2}{2} \lesssim \frac{1}{4} .$$

The first relationship stems from the fact that where $g(1,2)$ has an appreciable value, near $x_2' = 0$, $g(1,2)$ is somewhat more gently varying than $e^{-\delta^2 q^2}$. The second is obtained by inspecting Fig. 2.

Therefore, we have

$$\left[H'_{(1)}\right]_{123} \lesssim \frac{-\frac{h^2}{2m} 2 \int dx_2 dx_1 \left(\frac{-1}{4} .1 \ A^{-2}\right) \ \chi_{12}^2 \ g(12)}{\int dx_2 dx_1 \ \chi_{12}^2 \ g(1,2)}$$

$$\approx \frac{16 \times .1}{4} \lesssim .4 \ ^\circ K$$

There are 4 such pairs. Hence $H' \lesssim 1.6^\circ$ K.

In a similar fashion, we can estimate the second term of (F-1). Because the atoms are localized near lattice sites in an ordered lattice, but the summation over k yields only the single term where $\vec{s}_{ik} = -\vec{s}_{ij}$. Putting $i = 1$, $j = 2$, $k = 3$, and using the same approximations as in (F-7), we get

$$\left[H'_{(2)}\right]_{12} = -\frac{h^2}{2m} \ \frac{1}{A} \int \frac{\vec{s}_{12} \cdot \vec{s}_{13}}{r_{12} \ r_{13}} \ \frac{\partial}{\partial r_{12}} \frac{\partial}{\partial r_{13}} \chi_{12}^2 \ \chi_{13}^2 \ \chi_{32}^2$$

$$\times \prod_{t \neq 1,2,3} \chi_{1t}^2 \ \chi_{2t}^2 \ \chi_{3t}^2 \ \cdot \ d\vec{X}_1 d\vec{X}_2 d\vec{X}_3$$

$$= -\frac{h}{2m} \frac{1}{A} \int -(3\cdot 4)^2 \ (.1)^2 \ \chi_{12}^2 \ \chi_{13}^2 \ \chi_{32}^2 \ \prod_t \ \chi_{1t}^2 \ \chi_{2t}^2 \ \chi_{3t}^2 \ d\vec{X}_1 \ d\vec{X}_2 \ d\vec{X}_3$$

$$\approx + \frac{16}{2}\,(11)\,(.01) = .8$$

There are four such pairs per atom, so that $H'_{(2)} \approx 3.2°\ K$.

The estimating procedure used here demonstrates only that H' is not the dominant term in the energy. The assumption that H' is small and has little effect on the wave function must remain an assumption of this theory.

APPENDIX C

THE CORRELATION ENERGY MATRIX ELEMENT

In this appendix we obtain the factor 1/3 introduced into the energy in Eq. IV-(27) by a more detailed study. In Eq. IV-(27) the matrix element $(\prod_t \sqrt{f_t}\,,\,(T_1 \sqrt{f_j}\,) \prod_{k\neq j} \sqrt{f_k})$ measures a "kinetic energy" of particle 1, using $\sqrt{f_j}$, the part of the wave function of particle 1 which is determined by correlations with particle j. The sum of all such contributions is the sum total of the single particle energy resulting from the confining correlations. In mathematical symbols, $T_1 \sqrt{f_j}$ is $-\frac{h^2}{2m} \frac{\partial^2}{\partial \Delta_{1j}^2} \sqrt{f_j}$.

Let us set up a coordinate frame with x_j parallel to R_{1j}, so that $T_1 \sqrt{f_j} = -h^2/2m\, \partial^2/\partial x_j^{\,2} \sqrt{f_j}$. Let us further assume that our symmetry is such that there are two more atoms, say k and t, at the same distance R_λ, but on the y_j and z_j axes. The kinetic energy associated with correlations of 1 with these three atoms is then

$$\langle T \rangle_{1,jkt} = \left[-\frac{h^2}{2m} \left[\sqrt{f_j}\, \frac{\partial^2}{\partial x_j^{\,2}} \sqrt{f_j} \prod_{m\neq j} f_m + \sqrt{f_k}\, \frac{\partial^2}{\partial y_j^{\,2}} \prod_{m\neq k} f_m \right.\right.$$

$$\left.\left. + \sqrt{f_t}\,,\, \frac{\partial^2}{\partial z_j^{\,2}} \sqrt{f_t} \prod_{m\neq t} f_m \right]\right] . \qquad \text{(C-1)}$$

We can write the same expression for two other sets of axes, $x \to y$, and $x \to z$, add the three results, and divide by 3.

$$\langle T\rangle_{1,jkt} = \frac{1}{3}\left(-\frac{h^2}{2m}\right)\Bigg(\sqrt{f_j}, \left(\frac{\partial^2}{\partial x_j^{\,2}}+\frac{\partial^2}{\partial y_k^{\,2}}+\frac{\partial^2}{\partial z_t^{\,2}}\right)\sqrt{f_j}\prod_{m\neq j} f_m$$

$$+\sqrt{f_k}, \left(\frac{\partial^2}{\partial x_k^{\,2}}+\frac{\partial^2}{\partial y_t^{\,2}}+\frac{\partial^2}{\partial z_j^{\,2}}\right)\sqrt{f_k}\prod_{m\neq k} f_k$$

$$+\sqrt{f_t}, \left(\frac{\partial^2}{\partial x_t^{\,2}}+\frac{\partial^2}{\partial y_j^{\,2}}+\frac{\partial^2}{\partial z_k^{\,2}}\right)\sqrt{f_t}\prod_{m\neq t} f_m\Bigg). \qquad \text{(G-2)}$$

But in our single-particle representation, all the f's for atoms at the same distance R_λ are spherically symmetric about the origin, lattice site 1. The subscripts on the derivatives are then superfluous. We can, therefore, write, for (G-2),

$$\langle T\rangle_{1,jkt} = -\frac{h^2}{2m}\,\frac{1}{3}\Bigg(\sqrt{f_j}\;\nabla^2\sqrt{f_j}\prod_{m\neq j} f_m + \sqrt{f_k}\;\nabla^2\sqrt{f_k}\prod_{m\neq k} f_m$$

$$+\sqrt{f_k}\;\nabla^2\sqrt{f_k}\prod_{m\neq k} f_m\Bigg)$$

$$= \frac{1}{3}\prod_j\sqrt{f_j(\vec{r}_j)}\;\nabla^2\prod\sqrt{f_j(\vec{r}_j)} \qquad \text{(G-3)}$$

Writing (G-3) for all the atoms in all the rings, and normalizing we have

$$\langle T\rangle_1 = \frac{\int -\frac{h^2}{2m}\,\frac{1}{3}\,\nabla^2\, e^{-\frac{q_1'^2 s^2}{2}}\; e^{-\frac{q_1^2 s^2}{2}}\,dv}{\int e^{-q_2 s^2}\,dv} \qquad \text{(G-4)}$$

We can understand the factor 1/3 in another way, by applying classical mechanics and then identifying the dynamical variables with the corresponding quantum-mechanical operators.

In the diagram, we have q_1, measuring the displacement $\bar{u}_j$ of the particle 1 from the lattice sites j, by the relationship $\vec{u}_j = \vec{q}_1 - \vec{R}_{1j}$, or equivalently,

$$u_j^2 = q_1^2 + R_j^2 + 2q_1 R_j \cos \theta_j. \tag{G-5}$$

We wish to measure the kinetic energy of the particle 1 by observing the lengths of all the u_j and taking a suitable average. Let us assume that we cannot measure our absolute position in space, but merely can measure the scalar quantities u_j^2. (The problem we wish to study is the inverse one, where we measure quantities in terms of q, and deduce the corresponding quantities in u_j.)

We proceed by taking the time derivative of (G-5) and squaring:

$$2q\dot{q} - 2q R \cos \theta_j - 2q R \dot{\overline{\cos \theta}} = 2\, u_j\, \dot{u}_j$$

$$q^2 \dot{q}^2 + \dot{q}^2 R^2 \cos \theta_j + q^2 R^2 (\dot{\overline{\cos \theta}}_j)^2 - 2q\dot{q}^2 R \cos \theta_j$$

$$- q^2 \dot{q} R \dot{\overline{\cos \theta}}_j + 2 \dot{q} q R^2 \cos \theta_j \dot{\overline{\cos \theta}}_j = \dot{u}_j^2 u_j^2 .$$

Summing over j and averaging u_j, q, and $\dot{q}$ over time, and observing that u_j is nearly constant and equal to R_j, we get

$$n_j\, q^2\, \dot{q}^2 + n_j\, \dot{q}^2\, R_j^{\,2}\, \frac{1}{3} + q^2\, R^2\, n_j \left\langle \overline{\dot{\cos\theta_j}^{\,2}} \right\rangle = \sum_j R_j^{\,2}\, \dot{u}_j^{\,2}.$$

Divide by $R_j^{\,2}$:

$$n_j\, \dot{q}^2\, \frac{1}{3} + q^2\, n_j \left(\frac{\dot{q}^2}{R_j^{\,2}} + \left\langle \overline{\dot{\cos\theta}} \right\rangle^2 \right) = \sum_j u_j^{\,2}\ .$$

For small q, or low angular momentum, we get

$$n_j\, \dot{q}^2\, \frac{1}{3} = \sum_j \dot{u}_j^{\,2}$$

or

$$\frac{m\,\dot{q}^2}{2} = 3 \times \frac{m}{2}\ \frac{\sum_j \dot{u}_j^{\,2}}{n_j}\ .$$

The kinetic energy is three times the average of the "kinetic energies" relative to the fixed points.

In our case, we ask for the apparent kinetic energy of relative motion to a set of points j, in terms of the kinetic energy of a particle moving in a path described by q,

$$\frac{1}{3} \times \frac{m\,\dot{q}^2}{2} = \frac{1}{n_j} \sum_j \frac{m\,\dot{u}_j^{\,2}}{2}\ . \qquad \text{(C-6)}$$

By the correspondence principle, the right side of (C-6) represents the "effective kinetic energy" of Eq. IV-(26), and the left side represents the modified kinetic energy of IV-(27). We are, therefore, led to the factor 1/3.

APPENDIX H

NORMALIZATION OF THE WAVE FUNCTION

In this appendix we attend to the detailed problem of normalizing the ground state wave function.

In Chapter IV, we found that the expression

$$\gamma(1) = A \sum_i |\phi_i(1)|^2 \prod_k \int \gamma(k)\, \chi^2_{1k}(r_{1k}) d\vec{x}_k$$

could be written in the form $\gamma(1) = \sum_j \gamma_j(1)$, where

$$\gamma_1(1) = e^{-\alpha^2 q^2} e^{-\delta_0^2 q^2} .$$

Here $\delta_0^2 = -\frac{1}{q^2} \ln \prod_k \int \gamma(k)\, \chi^2_{1k}(r_{1k}) d\vec{x}_k$, a quantity which we can obtain by a lattice sum, and

$$e^{-\alpha^2 q_1^2} = \lim_{\vec{r}_1 \to \vec{R}_1} A \sum_i |\phi_i(1)|^2 \tag{H-1}$$

We must estimate α^2 to determine its effect on $\gamma_1(1)$, and this necessity leads us into the determination of A, and the detailed form of the ϕ_i.

The $\phi_i(\vec{X}_j)$ are a set of functions which are eigenstates of our zero order Hamiltonian. These states are occupied only because we must satisfy the Pauli principle.

Since the variable $\vec{X}_j$ does not appear in H_0, the labels i on $\phi_i(\vec{X}_j)$ are good quantum numbers, and, in a way exactly parallel to

the treatment of the shell model, we call upon them to describe the states permitted by the Pauli principle. Each of these states we will assume to be occupied by two, one, or no particles. (We label the states by ℓ and get two particles per state in our modified scheme, rather than by $j = \ell \pm 1/2$, for one particle per state in the usual scheme.) Then, since the particles are kept in the vicinity of lattice sites, each wave must be of a wavelength sufficient to span two lattice sites.

In Chapter IV, we wrote a general set of waves for a simple cubic lattice

$$\phi_i \rightarrow C_{ijk} \cos\left(\frac{\pi x}{n_i a} + \beta_{n_i}\right) \cos\left(\frac{\pi y}{n_j a} + \beta_{n_j}\right) \cos\left(\frac{\pi z}{n_j a} + \beta_{n_k}\right) \tag{H-2}$$

where the β_{n_i} were chosen for each wave to put no nodes at lattice points, and for n or $1/n$ odd, to place maxima at lattice points, or for n or $1/n$ even, maxima midway between lattice points.

We will now evaluate A in a particular case, where the lattice point $\vec{R}_1$ is at the center of a solid $(N_x\, a)$ by $(N_y\, a)$ by $(N_z\, a)$. In this case,

$$\phi_i \rightarrow C_{ijk} \prod_{\substack{u=x,y,z \\ n_u = n_i, n_j, n_k}} \cos \frac{\pi u}{n_u a} \tag{H-3}$$

$$n_u = 1, 3, 5, \ldots (N)^{1/3}.$$

We evaluate A by writing

$$\int r_1(1)\, d\vec{X}_1 = A \int \sum_i |\phi_i(1)|^2 \prod_k \int r_k(k)\, X^2_{ik}\, d\vec{x}_k$$

$$= A \int \sum_{ijk} C^2_{ijk} \prod_u \cos^2\left(\frac{\pi\, u}{n_u a}\right) e^{-\delta_0{}^2 q_1{}^2} \sqrt{\frac{\delta_0{}^2}{\pi}}^{\,3}\, d\vec{X}_1 \,. \tag{H-4}$$

We have learned that $e^{-\delta_0{}^2 q_1{}^2}$ is fast-varying compared to the lattice spacing. Hence, all the $\cos^2$ terms can be taken to be unity, and we get

$$\int r_1(1) d\vec{X}_1 = 1 = A \sum_{ijk} C^2_{ijk} \,,$$

or

$$A = \frac{1}{\sum_{ijk} C^2_{ijk}} \tag{H-5}$$

We now use IV-(34) to estimate α

$$\lim_{\vec{r}_1 \to \vec{R}_1} A \sum_i |\phi_i(r_1)|^2 = e^{-\alpha^2 q_1^{\,2}}$$

We will estimate α for the case leading to the waves (H-3). Using the lowest terms in the expansion of $\cos^2(x)$, we get

$$e^{-\alpha^2 q^2} = \frac{1}{\sum_{ijk} C^2_{ijk}} \sum_{ijk} \left[C^2_{ijk} \prod_{\substack{u=x,y,z \\ n_u = n_i, n_j, n_k}} \left(1 - \frac{u^2 \pi^2}{2\, n_u^{\,2}\, a^2}\right)\right] \tag{H-6}$$

We cannot evaluate the sums in (H-6) unless we know more about the relative values of the C_{ijk}. We now show that, if we use the assumptions preceding (H-2), (H-6) takes on a particularly simple form because the C_{ijk} are all of the same magnitude.

We write the N body density matrix in a slightly different form:

$$\Gamma^{(N)} = \sum_P P_s \, |\phi_1(1)|^2 \, [\chi_{12}(r_{12}) \, \chi_{13} \, \chi_{14} \cdots] \, |\phi_2(2)|^2$$

$$[\chi_{21}(r_{21}) \, \chi_{23} \, \chi_{24} \cdots] \, |\phi_3(3)|^2 \, [\chi_{31}(r_{31}) \, \chi_{32} \, \chi_{34} \cdots]$$

$$\cdots \, |\phi_N(N)|^2 \, [\chi_{N1} \, \chi_{N2} \cdots \chi_{N\,N-1}]. \qquad \text{(H-7)}$$

In (H-7), we again neglect overlap. We, therefore, have

$$\int \Gamma^{(N)} \, d\vec{X}_1 \, d\vec{X}_2 \cdots d\vec{X}_N = 1$$

$$= N! \int \phi_a(1)| \, [\chi_{12} \cdots \chi_{1N}] \, |\phi_b(2)|^2 \, [\chi_{23} \cdots \chi_{2N}]$$

$$|\phi_c(3)|^2 \, [\chi_{31} \cdots \chi_{3N}] \cdots |\phi_n(N)|^2$$

$$[\chi_{N1} \cdots \chi_{N\,N-1}] \, d\vec{X}_1 \, d\vec{X}_2 \, d\vec{X}_3 \cdots d\vec{X}_N \qquad \text{(H-8)}$$

Because each state is occupied to the same extent as any other state, in the way we write (H-7) and (H-8), all the permutations give the same value. In (H-8) we have written a particular one, and multiplied by the number of permutations.

We learned in Chapter IV that the correlations functions χ_{ij} can be treated to a good approximation as having one of the members of the pair fastened down to a lattice site. Then the product $[\chi_{12}\chi_{13}\chi_{14} \cdots \chi_{1N}]$ is the square root of the lattice product $\prod_k \chi^2(u_{1k})$, which we evaluated in Chapter IV as F_1.

We can write F_1 in a form which is general, for the entire solid, provided that $\delta^2 >> \frac{1}{a^2}$:

$$F_1 = \sum_j \prod_\lambda [X^2(R_\lambda)]^{n_\lambda} \; e^{-\delta_0^2 [\vec{R}_j - \vec{r}_1]^2}$$

Since only one member of the sum has any appreciable value, because of our assumption of no overlap, we can write

$$\sqrt{F_1} = \sum_j \prod_\lambda [X^2(R_\lambda)]^{n_\lambda/2} \; e^{-\frac{\delta_0^2}{2} [\vec{R}_j - \vec{r}_1]^2}$$

We, therefore, can write (H-8) in the following form

$$1 = N! \prod_k \int |\phi_k(1)|^2 \prod_\lambda [X(R_\lambda)]^{n_\lambda} \; e^{-\frac{\delta_0^2}{2} [\vec{R}_1 - \vec{r}_1]^2} \qquad \text{(H-9)}$$

Here, we have taken advantage of the fact that only the single member of the sum over j, where $\overline{R}_j = \overline{R}_1$, gives any contribution. Each of the states k is equally populated with two particles, hence $k = 1, 2 \ldots \frac{N}{2}$ and all the N integrals are equal. Because of the fast varying Gaussian function, each of the cosines in $\phi_k(1)$ is practically unity in this integral. Therefore, we have

$$1 = N! \prod_{i,j,k} \int C_{1jk}^2 \prod_\lambda [X(R_\lambda)]^{n_\lambda} \; e^{-\frac{\delta_0^2}{2} (\vec{R}_1 - \vec{r}_1)^2} \, dv_1 \, .$$

Define $\prod_\lambda [X(R_\lambda)]^{n_\lambda} = \beta(a)$

$$\sqrt[N]{1} = \sqrt[N]{N!} \; C_{1jk}^2 \; \beta(a) \; \sqrt{\frac{\pi\, 2}{\delta_0^2}}^{\,3}$$

or

$$C_{ijk}^2 = \frac{\delta_0^{\ 3}}{(2\,\pi)^{3/2}(N!)^{1/N}} = \frac{\delta_0^{\ 3}\, e}{(2\,\pi)^{3/2}\, N\, \beta(a)} \; .$$

Hence all the C_{ijk} are equal, and given by $(\delta_0^{\ 3}\, e/[(2\pi)^{3/2}\, N\, \beta(a)])^{1/2}$ $= C_0$. The numerical value of C_0 will not be useful to us. However, the fact that the C_{ijk} are all equal, within our assumptions, is of value.

We rewrite (H-6), using C_0 for all the C_{ijk}'s

$$e^{-\alpha^2 q^2} \cong \frac{1}{C_0^{\ 2} N}\; C_0^{\ 2} \sum_{ijk}\left[1 - \frac{\pi^2}{2a^2}\left(\frac{x^2}{n_i^{\ 2}} + \frac{y^2}{n_j^{\ 2}} + \frac{z^2}{n_k^{\ 2}} \right)\right] \qquad \text{(H-10)}$$

We have taken the leading terms in the product. (The expansion we use in (H-10) is expected to be valid, since $e^{-\delta^2 q^2}$ will provide a cut off in the region of poor convergence.)

In the sum of (H-10), there are $2(N)^{2/3}$ terms with $n_i = 1$, $2(N)^{2/3}$ terms with $n_i = 3$, etc. This comes about because the quantities $1/n_i$, $1/n_j$, $1/n_k$ are proportional to the components of a vector in the reciprocal lattice of our assumed simple cubic lattice. There are $N_y \times N_z = (N)^{2/3}$ lattice points in the plane $n_i = (\text{const})$ and an equal number in the reflected plane.

We can therefore rewrite (H-10)

$$e^{-\alpha^2 q^2} = \frac{1}{N}\left(N - \frac{2\pi^2}{2a^2}\left[x^2 \left(\frac{1}{1} + \frac{1}{9} + \frac{1}{25} + \ldots \frac{1}{N} \right) N^{2/3} \right.\right.$$

$$\left.\left. + \, y^2\, N^{2/3} \left(\frac{1}{1} + \frac{1}{9} + \frac{1}{25} + \ldots \frac{1}{N} \right) + z^2\, N^{2/3} \left(\frac{1}{1} + \ldots \frac{1}{N} \right) \right] \right) .$$

But $\frac{1}{1} + \frac{1}{3^2} + \frac{1}{5^2} + \cdots = \left(\frac{1}{1} + \frac{1}{2^2} + \frac{1}{3^2} + \cdots\right) - \frac{1}{4}\left(\frac{1}{1} + \frac{1}{2^2} + \frac{1}{3^2}\right)$

$$= \frac{3}{4}\,\frac{\pi^2}{6} = \frac{\pi^2}{8}$$

for large N. Hence

$$e^{-\alpha^2 q^2} = \frac{1}{N}\left[N - \frac{N^2\,3\,\pi^2}{a^2}\;\frac{\pi^2}{8}\left((x^2+y^2+z^2)\right)\right] \cong e^{-\frac{\pi^4 q^2}{8\cdot N^{1/3}\,a^2}}$$

or

$$\alpha \approx \frac{\pi^2\sqrt{2}}{4\,N^{1/6}\,a} \qquad \text{(H-11)}$$

In Eq. IV-(55), we stated that the contribution to the energy from the waves $\sum_i |\phi_i(1)|^2$ is:

$$\langle T\rangle_\alpha = -\frac{\hbar^2}{2m}\,\frac{\int \sum_i \phi_i(1)\,\nabla_1^2\,\phi_i(1)\,e^{-\alpha^2 q_1^2}\,d\vec{r}_1}{\int \sum_i |\phi_i(1)|^2\,e^{-\alpha^2 q_1^2}\,d\vec{r}_1} \qquad \text{(H-12)}$$

and is of order $N^{-1/3}$. We now show this explicitly. Using the representation (H-2), we have

$$\langle T\rangle_\alpha = -\frac{\hbar^2}{2m\,A_1}\int \frac{C_0^2\,\pi^2}{a^2}\left[\sum_{ijk}\left(\frac{1}{n_i^2} + \frac{1}{n_j^2} + \frac{1}{n_k^2}\right)\right]$$

$$\cos^2\left(\frac{\pi x_1}{n_i a}\right)\cos^2\left(\frac{\pi y_1}{n_j a}\right)\cos^2\left(\frac{\pi z_1}{n_k a}\right)\,e^{-\alpha^2 q^2}\,d\vec{r}_1\,.$$

where we have set the integral in the denominator of (H-12) equal to A_1.

As we did in (N-4), we can take all the cosines to be unity. We then get:

$$T_\alpha = - \frac{\hbar^2}{2m} \frac{\pi^2}{a^2} \frac{\sum\limits_{ijk} \left(\frac{1}{n_i^2} + \frac{1}{n_j^2} + \frac{1}{n_k^2} \right)}{\sum\limits_{ijk} (1)} .$$

Again, the sum $\sum\limits_{ijk}$ has N terms. Using $1/1 + 1/3^2 + 1/5^2 + \ldots = \pi^2/8$, we have

$$T_\alpha = \frac{- \frac{\hbar^2}{2m} \frac{\pi^2}{8} N^{1/3} N^{1/3} 3 \pi^2}{N^{1/3} N^{1/3} N^{1/3} a^2}$$

$$= - \frac{\hbar^2 \pi^2 3 \pi^2}{16 m N^{1/3} a^2} .$$

GLOSSARY

S.P.O.	Single Particle Orbital
B.P.	N. Bernardes and H. Primakoff, Phys. Rev. 119, 968 (1960)
$\vec{r}_i$	The position coordinates of particle i, not including spin ζ_i ($\vec{X}_i$ includes spin)
$\vec{X}_i$	The coordinates of particle i, including spin ζ_i ($\vec{r}_i$ does not include spin)
°K	Degrees Kelvin
Å	Angstrom unit
$\sum_P P$	Forms a Slater determinant of what follows. The permutation operator for Fermi particles
$\sum_P P_S$	Forms a symmetric permutation of what follows.
$\sum_P P_i$	Permutes only the coordinate indices i, in the anti-symmetric sense.
$\delta(x)$	Dirac δ function
δ	The "wave number" of the single particle representation $\gamma(i) = \text{const}\; e^{-\delta^2 q_i^2}$, q_i = distance from lattice site i.
$f_j(u_{jk})$	$\int \gamma(j)\, \chi^2_{kj}(r_{kj})\, d\vec{r}_j$
$\Gamma^{(p)}(\vec{X}_1' \vec{X}_2' \dots \vec{X}_p' \mid \vec{X}_1\, \vec{X}_2 \dots \vec{X}_p)$	Density matrix of order (p) (See Chapter IV.)
$\gamma(\vec{X}' \mid \vec{X}_1)$	Density matrix of order 1. (See Chapter IV.)
$\bar{s}_{ij}$	The displacement between particle i and particle j. This variable has a derivative $\partial/\partial x$, but no derivative $\partial/\partial r_{ij}$.

r_{ij} — The interparticle parameter, which is an independent variable in the Pluvinage formulation of the Schrodinger equation. It has the constraint

$$r_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2} = \sqrt{\vec{s}_{ij} \cdot \vec{s}_{ij}} ,$$

which must be imposed when evaluating matrix elements containing r_{ij}. There is a derivative of r_{ij}, $\partial/\partial r_{ij}$ but no derivative $\partial/\partial x$.

$\vec{t}_{ij}$ — The position of the center-of-mass of particles i and j. There is a derivative $\partial/\partial x$, but no derivative $\partial/\partial r_{ij}$.

$\chi_{ij}(r_{ij})$ — The correlation function, defined by formula III-(17). It has a series representation $F_0(\sigma/r_{ij})\, \theta(r_{ij} - r_0)$, where θ is the step function, and a Yukawa-type representation, $1 - r_0/r \; e^{-\gamma(r - r_0)}$.

u_{kj} — The distance from the field point k to the lattice point j.

$\phi_i(\vec{X}_j)$ — The single-particle wave function, a function of space and spin.

$\phi_i(\vec{r}_j)$ — The single-particle wave function, a function of space only.

$\phi(x)$ — The error integral $\phi(x) = (2/\pi^{1/2})\int_0^x e^{-t^2}\, dt$.

F_t — $\prod_j f_j(u_{tj})$, where t is the position of an atom near lattice point t.

$F_0(x)$ — A series expression for χ, the correlation function.

$F(r_{ij})$ — An arbitrary function of (r_{ij}).

Δ_j — $|\vec{u}_{ij}| - |\vec{R}_{ij}|$ (See Fig. 4.)

g_λ $\quad \left[\frac{1}{u} + \frac{1}{2} \frac{d}{du} \right] \left. \frac{f'(u)}{f(u)} \right]_{R_\lambda}$

R_λ $\quad$ The distance from the lattice point denoting the single-particle reference point to the shell of atoms at distance R_λ, a function of lattice geometry. (See Fig. 4.)

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